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Surface characterization of latexes and latex rheology

Syed Mahmood Ahmed
Lehigh University

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A Research Report

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CERTIFICATE OF APPROVAL

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

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ABSTRACT

Monodisperse polystyrene latexes were prepared and the number of chemically bound surface endgroups were determined. These strong acid surface groups were presumably sulfate. These sulfate surface groups were converted to carboxylic groups by an oxidation reaction.

After cleaning the latexes by dialysis and ion-exchange, the latex particle surfaces were characterized by conductometric titration before and after oxidation. The conductometric titration technique was used successfully to determine acidic group concentrations of the order of 10^{-6} eq/gm of polymer.

Rheological measurements were obtained for the original latexes, the cleaned latexes, and the latexes after oxidation and cleaning. The original latexes (with sulfate and hydroxyl groups on the surfaces) and the latexes after oxidation (with sulfate and carboxyl groups on the surfaces) were Newtonian, while cleaned latexes with sulfate and hydroxyl groups on their surfaces were non-Newtonian and showed an increase in viscosities due to the secondary electroviscous effect.

This behavior was observed because latex particles with sulfate and hydroxyl groups on their surfaces had an expanded electrical double layer on ion exchange, while latex particles with sulfate and carboxyl groups did not show this expansion of the double layer, as these carboxyl groups were undissociated.

INTRODUCTION

Synthetic latexes are aqueous dispersions of polymers which are often produced by emulsion polymerization, a free radical addition polymerization process. A water-immiscible monomer is emulsified in water using an oil-in-water emulsifier and polymerized using a free radical initiator.

Latex particles are spherical and of colloidal size. These may be monodisperse or polydisperse. Monodisperse latexes are ideal models for colloidal studies provided their surfaces are well-characterized. These monodisperse latexes also provide a convenient system for investigating the rheological properties of suspension of spherical particles. Latex particles are near-perfect spheres and do not deform under the experimental stresses applied for the study of rheological behavior. The availability of monodisperse latexes of different sizes allows a study of particle size effect on rheology. Also the rheological properties of latexes themselves are very important from theoretical as well as practical viewpoints. Viscosity plays a very important role in the processing and in the application of these latexes and thus, control of viscosity can be important.

The most work done in this field, so far, deals with the viscosity concentration relationships, their non-Newtonian behavior, and the effects of electrolyte on the rheology. No work has been done to check whether there is any influence, on the rheological behavior, of the surface polymer endgroups of different nature and their counterions.

In the present work, we studied the influence of different chemically-bound surface endgroups on the rheology and the effect of different counterions on the expansion of electrical double layers after ion exchange of the latexes.

II. RHEOLOGICAL BEHAVIOR OF LATEXES

Einstein's theory of viscosity of dilute dispersions of rigid spheres is applicable to some dilute latex systems. Einstein's equation relates the relative viscosity with volume fraction as follows:

$$\eta_\gamma = 1 + 2.5\phi \qquad (1)$$

where $\eta_\gamma = \frac{\eta}{\eta_o}$ = relative viscosity

η = viscosity of suspension

η_o = viscosity of the medium

ϕ = volume fraction of the spheres in the suspension.

The intrinsic viscosity is defined as:

$$[\eta] = \lim_{\phi \to o} [\eta_\gamma - 1]/\phi \qquad (2)$$

According to Einstein's equation, $[\eta]$ is equal to 2.5 regardless of the size or size distribution of the spheres. A typical viscosity-concentration curve following Equation 2 is shown in Figure 1. The initial slope of this curve is the intrinsic viscosity. ϕ_{max}, in the figure, is the volume fraction of the spheres in the suspension at which the viscosity becomes infinite. At this volume fraction, the dispersed particles lock into a rigid structure and flow ceases.

The Einstein equation is applicable only to the viscosity of dilute latexes with intrinsic viscosities very close to 2.5. Much work has been done to extend Einstein's theory to suspension of finite concentrations. About 100 different equations are reported in the literature (1,2) which describe the viscosity concentration behavior of latexes. Some of these will be discussed below.

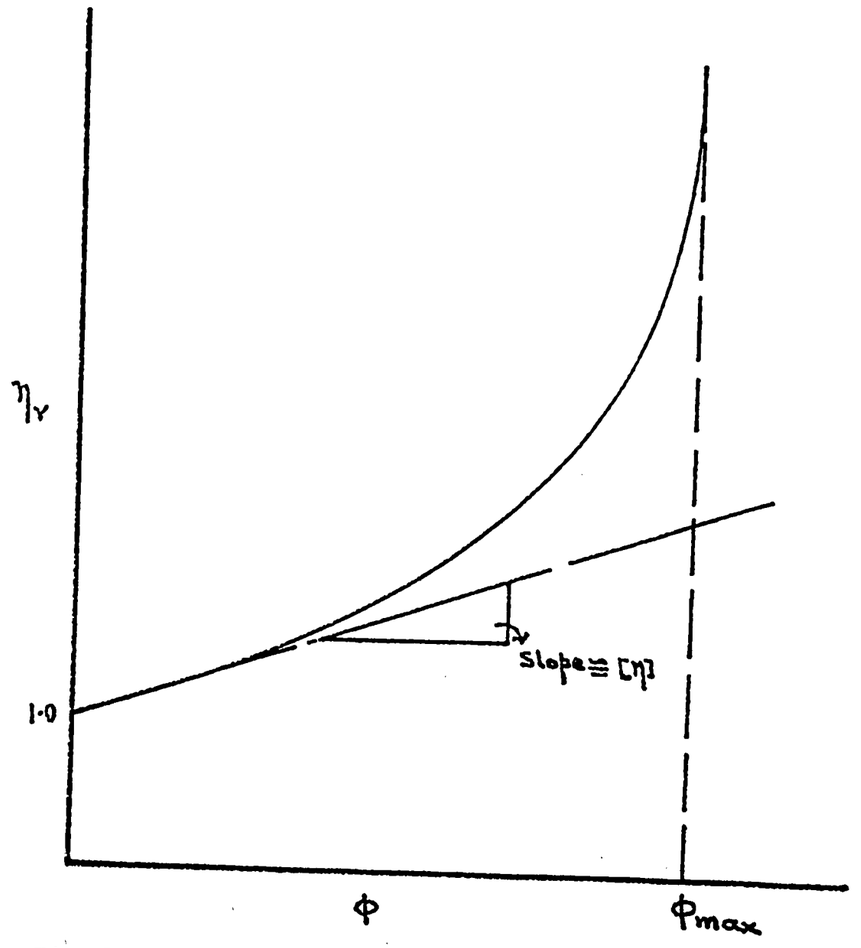


Fig. 1. Typical Viscosity-Concentration curve.

At finite concentration, the relative viscosity can be expressed in terms of power series in ϕ

$$\eta_\gamma = 1 + k_1\phi + k_2\phi^2 + k_3\phi^3 + \ldots\ldots \qquad (3)$$

where η_γ is the relative viscosity

k_1 is the Einstein's coefficient

k_2, k_3 are higher-order coefficients.

These higher-order coefficients account for the particle-particle interactions. k_2 varies from 3 to 15 (5,8) and k_3 from 16 to 50. The difficulty in the application of this equation is that, with increasing concentrations, more higher-order terms are required and thus more coefficients must be determined. This is not easy to do accurately.

Eilers (3,4) used the following equation to relate the viscosity to concentration for suspensions of bitumen spheres:

$$\eta_\gamma = [1 + (\tfrac{1}{2}[\eta]\phi)/(1 - s\phi)]^2$$

where s is the self-crowding factor, and is equal to $\frac{1}{\phi_{max}}$

Maron et al. (5) gave the following relation for polydisperse synthetic latexes:

$$\eta_\gamma = \exp\,[[\eta]\phi/(1 - s\phi)]$$

Many closed-form type of equations relating the viscosity and concentration to cover the entire range of concentration have been proposed. One form is written as follows:

$$\eta_\gamma = (1 - s\phi)^{-N}$$

where N is a parameter that depends on the material.

Mooney (6) considered the effect of particle addition to an existing suspension. His equation is given as:

$$\ln \eta_\gamma = k_1 \phi / (1 - s\phi)$$

A similar equation was proposed by Dougherty and Krieger (7). It is given as

$$\eta_\gamma = [1 - \frac{\phi}{\phi_{max}}]^{-[\eta]\phi_{max}}$$

This equation reduces to the Eilers' form when the product of ϕ_{max} and $[\eta]$ is equal to two, if $[\eta] = 2.5$ and $\phi_{max} = .74$, then $\phi_{max}\ [\eta] = 1.85$. So Eilers' and Krieger's equations predict very similar behavior for dispersions of rigid spheres.

Particle size, particle size distribution, temperature and electrolyte concentration are the parameters that should be controlled during the experimental studies of viscosity-concentration relationships. Johnson and Kelsey (8) studied the effect of particle size and polydispersity on viscosity. Viscosity increases with decreasing particle size, and as the particle size distribution broadens, viscosity goes down. Due to important and difficult hydrodynamic problems, viscosity-concentration relationships that fit the actual experimental data better than the above equations have not yet been obtained.

Saunders (9) did a series of experiments with monodisperse polystyrene latexes of particle size from 99 to 871 nm. The experimental conditions were such that the latexes had complete surface coverage with the adsorbed emulsifier and the aqueous phase had a constant viscosity.

His results show that the viscosity-concentration relationship for monodisperse latexes up to a volume fraction of 0.35 obeys Mooney's equation and are Newtonian. Values of s vary from 1.118 to 1.357, increasing with decreasing particle size. The value of k_1 was more than 2.5 and increased with decreasing particle size but with a correction, considering the adsorbed emulsifier layer, in the volume fraction, as

$$\phi_e = \phi \left(1 + \frac{6\Delta}{D}\right)$$

where ϕ_e = effective volume fraction

Δ = monolayer thickness

D = particle diameter.

It was determined that the value of k_1 is independent of particle size and was equal to $2.504 \pm .046$.

Saunder's results also show that the viscosity increases as the particle size decreases.

Maron and coworkers did many experiments using different latexes and concluded that the latex viscosity behavior was non-Newtonian above a volume fraction of 0.25. This non-Newtonian behavior will be discussed in the following pages. The most common non-Newtonian behavior in latex systems is shear-thinning or pseudoplastic. Shear-thickening behavior is sometimes observed with compounded latexes.

Maron and Madow (10) studied the rhelogical behavior of 50:50 butadiene-styrene copolymer latex and found that up to 40% (by volume) solids the shear rate-shear stress relationship can be given by the

following equation:

$$\dot{\gamma}^N = \eta' \tau$$

where $\dot{\gamma}$ = shear rate sec^{-1}

τ = shear stress $dynes/cm^2$

N and η' are constants which depend only on concentration at constant temperatures. They also found that above 40% solids, the shear rate-shear stress relationship needs two equations of the above form with N_1, η_1', and N_2, η_2' as constants. When log $\dot{\gamma}$ is plotted vs. log τ the two lines representing these two equations intersect each other. They found that the latex system was Newtonian up to $\phi = 0.25$ and for $\phi = 0.25$ to $\phi = 0.47$ its behavior was dependent on the applied shear stress. The latex was Newtonian when the shear stress was below the value it has at the intersection of the above said two lines. The latex was non-Newtonian when the shear stress was above this value. This latex was non-Newtonian above $\phi = 0.47$ regardless of the applied shear stress. With another, 70:30 butadiene-styrene copolymer, latex, they applied an extended form of Einstein's equation as follows:

$$\log \frac{\eta'}{\eta} = bZ$$

where Z is $\frac{\alpha\phi}{1 - \alpha\phi}$ applicable for $\phi = 0$ to 0.6.
This gives the Einstein constant α very close to 2.5 and ϕ_{max} about 0.74.

Maron and Fok (11) prepared an 84:16 butadiene-styrene copolymer latex at low temperature of polymerization compared to the two latexes

discussed above. Their studies showed that this latex could not be treated in its rheological behavior as the other two. They applied a modified form of Eilers' equation to this system in the following form:

$$\frac{\eta_\gamma^{1/2} - 1}{\phi} = \alpha + \beta(\eta_\gamma^{1/2} - 1)$$

where η_γ is defined as $(\tau/\dot{\gamma})/\eta_w$

η_w = viscosity of water and α and β are constants.

They also concluded from their work that the visocisity of this latex varied with temperature, mainly because of the changes in the viscosity of water with temperature and the non-Newtonian behavior is not an effect of temperature but is due to the applied shear stress and concentration of the system.

Maron and Pierce (12) applied a generalized flow theory (13) to the data of Maron and Fok discussed above. This theory holds for both Newtonian and non-Newtonian regions. Ree and Eyring considered a non-Newtonian system as consisting of a number of flow units and each of these units have different relaxation time and viscosity of a system having 'n' flow units is given as:

$$\eta = \sum_n \frac{\times_n \beta_n}{\alpha_n} \frac{\sin h^{-1} \beta\dot{\gamma}}{\beta\dot{\gamma}}$$

where $\times_n$ = fractional area occupied by the nth flow unit on the shear surface

$$\alpha_n = \frac{(\lambda\ \lambda_2\ \lambda_3)n}{2kT}$$

λ = distance a flow unit moves between equilibrium position

$\lambda_2 \lambda_3$ = cross sectional area of the flow units

k = Boltzmann constant

T = temperature

$$\beta_n = \frac{1}{[(\lambda/\lambda_1)^2 k']_n}$$

λ_1 = distance between planes of flow units of given kind

k' = rate constant for passage of a given flow unit over the potential energy barrier.

Maron and Pierce applied the above Ree-Eyring equation to the latex system, considering it as having two flow units, namely, water and polymer particles.

The generalized equation now becomes

$$\eta = \frac{x_1 \beta_1}{\alpha_1} + \frac{x_2 \beta_2}{\alpha_2} \frac{\sin h^{-1} \beta_2 \dot{\gamma}}{\beta_2 \dot{\gamma}}$$

The first term of the equation $\frac{x_1 \beta_1}{\alpha_1}$ represents the first flow unit, water, which is Newtonian and the second term represents the polymer particles. Maron and Pierce applied this equation successfully to previously discussed data of Maron and Fok, both in the Newtonian and non-Newtonian regions.

From all the above work, it is concluded that the non-Newtonian behavior comes with higher concentration of latex and this is because of the crowding or the interaction between the particles.

Krieger and coworker (13) developed a theory with main consideration about the interaction between neighboring particles and presented the following equation:

$$\frac{\eta - \eta_\infty}{\eta_o - \eta_\infty} = \left(1 - \frac{[\tau]}{\tau_c}\right)^{-1}$$

where η_o = viscosity at zero shear rate

η_∞ = viscosity at infinite shear rate

$\tau_c = \frac{\alpha\, kT}{3a^3}$

a = radius of particle

α = correction factor for the angle of rotation of dumbbell.

Latexes also display thixotropic (time-dependent) behavior. This behavior is very important for some of the latex products. For example, the quality of paints is very much dependent on their thixotropic behavior.

Mooney (6) made measurements on a commercial latex compound containing 47.5% latex solids, with a viscometer designed to maintain a uniform shearing stress and shear rate throughout the test material. Viscosity-time curves for various values of shear stress from his work are shown in Figure 2. Very little work has been done in the field of thixotropic behavior of latexes.

Electrical charges present at the particle surface can influence the rheology of latex systems and these are known as electroviscous effects. There are three electroviscous effects:

(1) An increment in the viscosity due to distortion of the electrical double layer under shear;

(2) An increase in the viscosity at finite concentrations due to coulombic interactions between the double layers of different particles; and

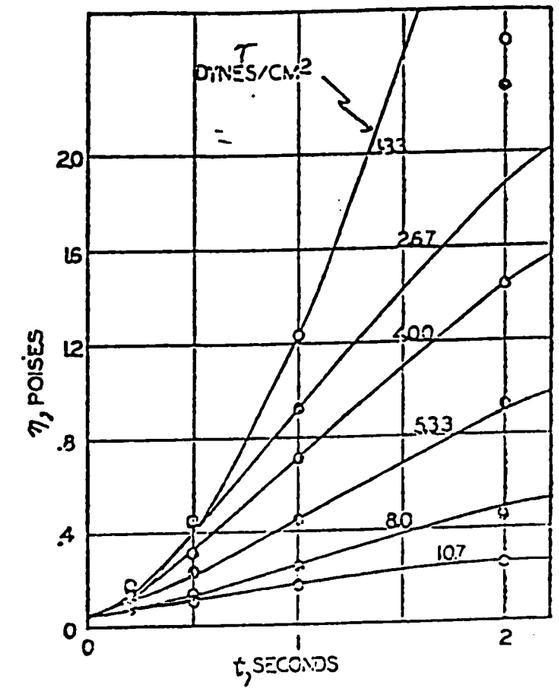


Fig. 2. Observed and Calculated Viscosity vs. Time after stirring for various values of τ, the traction. (6).

(3) Effects due to distortion of the particles themselves as a result of electrostatic forces arising from the presence of charges on the particle.

Fryling (14) and subsequently Brodnyan and Kelley (15,16) removed the free electrolyte from latexes by dialysis and measured the viscosity. They found that the viscosity changed by orders of magnitude. This large increase in the viscosity is because of an increase in the effective hydrodynamic radius of the particles caused by the increase in the thickness of the electrical double layer, which is sensitive to the surface charge and electrolyte content. When Brodnyan and Kelley (15,16) added the electrolyte back to the dialyzed latex, the viscosity was reduced to or below the original value. The dialyzed latex was non-Newtonian, but after the addition of electrolyte it became Newtonian again.

Harmsen et al. (17) gave an explanation for this second electroviscous effect based upon the increase in energy dissipation resulting from alterations of particle trajectories due to the presence of electrical charges which cause the particles to avoid one another.

Woods and Krieger (18) measured the viscosities of latexes with different levels of electrolyte to find a minimum in the viscosity-electrolyte relation. They revealed the following features:

(1) A strong electrolyte effect at low shear stress, which diminishes in magnitude as shear stress increases.

(2) A distinct maximum in viscosity which is independent of shear stress at a specific electrolyte level.

(3) A high-shear limiting viscosity which is independent of electrolyte content if the electrolyte level is below that which gives the minimum in viscosity.

Their results showed that the viscosity-polymer concentration relation follows Eilers' equation and also the Dougherty-Kreiger equation.

Vanderhoff and coworkers (19) cleaned latexes by an ion-exchange method and observed an increase in the viscosities of the latexes. The flow behavior of the original latex with a volume fraction of 0.15 was Newtonian but after ion-exchange of this latex the behavior was found to be non-Newtonian, even with a volume fraction of 0.0047. An addition of 10^{-3}M potassium nitrate changed the behavior to Newtonian again. Vanderhoff et al. also concluded from their studies that the increase in viscosity was due to the second electroviscous effect. They showed that the double layer expanded greatly when the electrolyte was removed by ion-exchange.

Wang (20) made a study of electroviscous effects in concentrated latexes. The effect of both shear rate and ionic strength were considered in terms of effective volume. His data follow Mooney's equation. The contribution of the ionic double layer to the effective volume fraction was estimated from the limiting Debye-Huckel equation and found to be higher at shear rates less than 100 sec^{-1} and less at shear rates above 1000 sec^{-1}. At infinite shear rate, the effect of the double layer vanishes.

Chan et al. (21) measured the viscosities of sulfonated polystyrene-divinyl benzene copolymer latexes at various ionic strengths. They found the Huggins interaction coefficient over these ionic strengths and concluded that it decreases with ionic strength.

Stone-Masui and Watillon (22) studied the viscosities of polystyrene latexes and compared their data with the existing theories for the first and second electroviscous effects. They found that their data approximately fits the predictions of Chan et al. (21).

Krieger and Equiluz (23) studied the second electroviscous effect using ion-exchanged monodisperse polystyrene latexes. They measured the non-Newtonian viscosities for volume fraction from 0.05 to 0.50 at various electrolyte concentration. Their results showed that cleaned latexes yield stresses which decreased with decreasing volume fraction, that is, the second electroviscous effect is a function of equivalent concentrations of added electrolyte. Changing the type and valence of the ions had little influence on the electroviscous effect. The limiting viscosity at high shear rate was independent of electrolyte con-concentrations.

III. SURFACE CHARACTERIZATION

The experimental objective of this research project was to study the influence of different latex particle surface groups on latex rheology. Therefore, the first step of these experiments was to characterize the surface of the sample latexes. Much work has been done in this field by many workers. The results of the work done in this area are discussed briefly in the following few pages.

After the polymerization, the aqueous phase of latex may contain emulsifier, residual initiator and its decomposition products, and buffer. There may be some physically adsorbed emulsifier molecules and chemically bound endgroups on the surface of the latex particles.

The first step in the process of characterization of latex particle surfaces is cleaning, that is, the removal of eumulsifier, electrolyte and inorganic salts from the aqueous phase and from the particle surface. The resulting latex will be stabilized by the chemically-bound endgroups. The nature and the number of these groups can be determined by suitable techniques.

Cleaning of the latexes is usually done either by dialysis or by ion-exchange or by the combination of these two. Dialysis is a very slow process and takes weeks and even months for complete removal of the adsorbed emulsifier. Many workers (14,15,19,26) have reported that only partial removal of emulsifier is possible by this method. However, few other reports (24,28) showed results achieving complete cleaning by dialysis.

Vanderhoff and coworkers used an ion-exchange method for cleaning of the latexes and to exchange the counterions from the surface groups.

This method insures the complete exchange of Na^+ and K^+ cations of the surface endgroups for H^+ ions. The ion exchange resins used were 20-50 mesh Dowex 50W-X8 and Dowex 1-X8 resins. These resins were conditioned separately by four or five successive exchanges between hydrochloric acid and sodium hydroxide to remove the soluble materials from the resins. Mixed resins were applied in batches for ion-exchange. In the mixture Dowex 50W was kept in hydrogen form and Dowex 1 in the hydroxyl form. Vanderhoff et al. (19) removed all of the excess emulsifier from their polystyrene latexes using these ion exchange resins and obtained a constant surface charge.

Ottewill and Shaw (24) used dialysis successfully. Recently published work of Stone-Masui and Watillon (25) reports the failure of both of these techniques in the complete removal of emulsifier and they found that some of the emulsifier remained adsorbed at the particle surface. Perhaps this is the only work which reported failure.

Cleaned latexes have been characterized by electrophoretic studies, conductometric titration, potentiometric titration, rheological measurements, etc. Electrophoretic studies and titration techniques are used most widely. Titration methods are very precise for determining the nature of the groups for materials in solution and suspensions and the results obtained by these methods can be interpreted very accurately. A comparison of conductometric and potentiometric titration shows that the interpretation of the conductometric titration curves is easier than those obtained by potentiometric titrations.

Vanderhoff et al. (19,26,27) characterized polystyrene latex particles using conductometric titration. They used polystyrene latexes prepared with potassium persulfate as initiator. The decomposition and initiation mechanisms were suggested to be as follows:

$$S_2O_8^{-2} \dashrightarrow 2SO_4^-\cdot$$

$$SO_4^-\cdot + M \dashrightarrow SO_4^-M\cdot$$

$$SO_4^-M\cdot + M \dashrightarrow SO_4^-MM\cdot$$

Finally for termination by combination the polymer molecules will be

$$SO_4^-MM \sim\sim\sim MMSO_4^-$$

Thus each polymer molecule would have two sulfate endgroups and the cleaned latexes are stabilized by the presence of these charged groups. The titration curves from Vanderhoff's work showed their presence and they found that there was an average of one charged group per polymer molecule which was half of the expected number. They suggested that some of the sulfate groups were buried inside the particle and some of the groups were in hydroxyl form which came through the hydrolysis of the sulfate ion radicals,

$$SO_4^-\cdot + H_2O \dashrightarrow HO\cdot + HSO_4^-$$

and the polymer molecules initiated by these hydroxyl groups were not charged and could not be determined by conductometric titrations. They converted these hydroxyl groups to carboxyl groups by an oxidation reaction (26) and calculated the number of these groups by conductometric

titrations. The total number of endgroups/polymer molecules thus determined was about two. Latexes characterized by these workers had only strong acid groups, the sulfate groups, and hydroxyl groups at the particle surface. On the other hand, Ottewill and Shaw and their coworkers (24,28,29) reported that their latexes had weak acidic groups at their surfaces, regardless of the initiator or emulsifier used for polymerization. They used electrophoresis and confirmed their results by potentiometric titration. They suggested the oxidation during polymerization to form carboxylic groups.

Stone-Masui and Watillon (25) studied different latex systems. They prepared latexes with and without emulsifiers. Their results showed that when the emulsifier was the salt of a strong acid, there were strong acidic groups at the particle surface. In the absence of emulsifier, they found only weak acidic groups when the pH of the polymerization was not controlled. When they controlled the pH during polymerization by potassium bicarbonate, they found both strong and weak acidic groups on the particle surface. Their conclusion was that the latex prepared with emulsifier had emulsifier groups at the particle surfaces and these adsorbed groups could not be taken away by ion-exchange method.

Everett and Gultepe (30) characterized some polystyrene latexes cleaned by dialysis and reported to have strong and weak acidic groups on the particle surfaces. The workers in this field reported conflicting results. The work done under this project, discussed later, showed that there were only strong acidic groups and some hydroxyl groups on the particle surface. This is in agreement with the previous results

of Vanderhoff and his coworkers. The only possible reason for this conflict is the difference in the recipes of polymerization. The sulfate groups are easily hydrolyzable to form hydroxyl groups, and hydroxyl groups are oxidized to carboxyl groups in the presence of heavy metal traces. Thus weak acidic groups would form during polymerization if the recipe has any heavy metal traces, otherwise the persulfate initiator will provide strong acidic ends to the polymer molecules.

IV. EXPERIMENTAL PROCEDURE

The objective of this research was to study the influence of different chemically bound surface groups on the rheological properties. Therefore, the first step was to determine the number of these surface groups and to study the rheological properties. The second step was to convert these groups to the other possible forms and to study the influence of these new groups on the rheology. Thus the experimental work can be divided into two parts:

(1) Characterization of the surfaces of the sample latex particles, and

(2) Rheological studies of such characterized latexes.

Experimental Systems

Monodisperse polystyrene latexes and a monodisperse styrene-butadiene copolymer latex were used for these studies. Particle size data are given in Table 1.

Cleaning of Latex

Cleaning was done by a combination of dialysis and ion-exchange. The original latexes were diluted to about 8 to 10% solids (by weight) with distilled, deionized water and then subjected to dialysis.

Dialysis was carried out in a Pope Scientific Inc. Multiple Dialyzer. The latex was suspended in cellophane dialyzing tubes and dialyzed against distilled-deionized water, the water being replaced every four hours during the day. After one week the latex samples were

TABLE 1

Experimental Systems.

Latex No.		Latex	Particle Diameter
1*	LS-1102-A	Polystyrene latex	190 nm
2*	LS-1074-B	Styrene-butadiene copolymer latex	210 nm
3*	LS-1134-B	Polystyrene Latex	300 nm
4**	--	Polystyrene latex	576 nm

* From Dow Chemical Company

** Prepared by the method of Kotera et al. (36)

removed from the dialysis tubes and subjected to ion-exchange.

The ion-exchange resins used were the 20-50 mesh Dowex 50W-X4 (the sulfonated salt of 96:4 styrene-divinylbenzene copolymer) and Dowex 1-X4 which was the analogous trimethyl ammonium salt. The resins were conditioned rigorously following the procedure given by Vanderhoff et al. (19) described below. The ion-exchange cleaning of the latex was accomplished by the batch method in which the dilute latex was mixed with excess of mixed resins under agitation for several hours. The latex was then separated from the resin beads by filtration through quartz wool and a small portion was removed for titration. The whole process, ion-exchange, filtration, titration, was repeated until a constant surface charge was obtained. For these latexes, beautiful rainbow color patterns were developed at the surface of the glass container after the latex had been cleaned. No soft glass was used in the experiments. It was noticed, during these cycles, that the surface charge increased at the end of each of the first few cycles, and it became constant for the rest of the cycles. This increase may have been due to incomplete exchange of Na^+ and K^+ ions in the beginning.

Conditioning of the Ion Exchange Resins

Ion-exchange resins may contain some soluble-polyelectrolytes, which can be leached during the process of ion exchange and dissolved in the latex, hence the complete removal of these leachable impurities is very important. The foregoing resins were cleaned using the method developed by Vanderhoff et al. (19) as follows.

The resins were washed separately with 85°C water and methanol until no more colored material was removed. The resins were then eluted consecutively with a three-fold excess of 3N sodium hydroxide, hot water, methanol, cold water, 3N hydrochloric acid, hot water, methanol and cold water. This cycle was repeated four times. The last cycle was completed by the slow elution of the Dowex 50W with a five-fold excess of 3N hydrochloric acid to convert it to the H^+ form and the Dowex 1 with a five-fold excess of 2N sodium hydroxide to convert it to the OH^- form. The resins were rinsed with distilled-deionized water and mixed by stirring. Before use they were washed again. The Dowex 50W was stored in H^+ form while Dowex 1 was stored in Cl^- form and converted to OH^- form only shortly before use.

The purity of the resins was monitored by measurements of wash water conductivity, surface tension, ultraviolet absorption (at 224 mμ) and acid or base required for neutralization of the water in which the resin was agitated for two hours. After conditioning the resins were agitated, separately, with water for two hours. Then the water was separated from the resins and UV absorption at 224 mμ was found to be negligible and conductivity was comparable with deionized water.

Conductometric Titrations

The conductometric titrations were carried out by recording the amplified voltage drop across a resistor in series with a conductivity cell while the ~0.02N NaOH was being added continuously from a constant rate burette. The titration apparatus was capable of recording the

specific conductance and pH of the latex under titration. The conductance channel of the recorder was calibrated with a standard KCl solution, and the pH channel of the recorder with 4.0, 7.0 and 10.0 pH buffer solutions. The automatic burette was set up to deliver the NaOH solution continuously at a constant flow rate of 0.8 ml per minute.

Immediately after starting the delivery of titrant (~0.02N NaOH) to the latex in the cell, the cell was jacked up such that the delivery tip of the burette was just immersed in the latex. Smooth conductometric titration curves resulted because of the better mixing of the titrant with the latex during titration. The diagram for the apparatus and a description of the parts is given in the equipment section.

Figures 3-6 show the conductometric titration curves for latexes 1-4, respectively, after constant surface charge is reached. From these curves it is clear that these latexes have only strong acidic groups) presumably sulfate) at the particle surface. This confirms the results of Vanderhoff et al. There were some hydroxyl groups present at the particle surface which were determined by oxidation, which will be discussed later. The next step of these experiments was to convert these sulfate endgroups to carboxyl groups by oxidation.

Latex samples were oxidized by following the procedure given by Vanden Hul and Vanderhoff (26) described below.

Weighed samples of latexes with known amounts of polymer were placed into capped bottles and heated for six hours at $90^{o}C$ with 0.1 to 0.3 gram of potassium persulfate per gram of polymer and $10^{-5}M$ silver nitrate as catalyst. The chemistry of this oxidation is shown below. It is carried out in two steps. The first step is the hydrolysis of sulfate groups

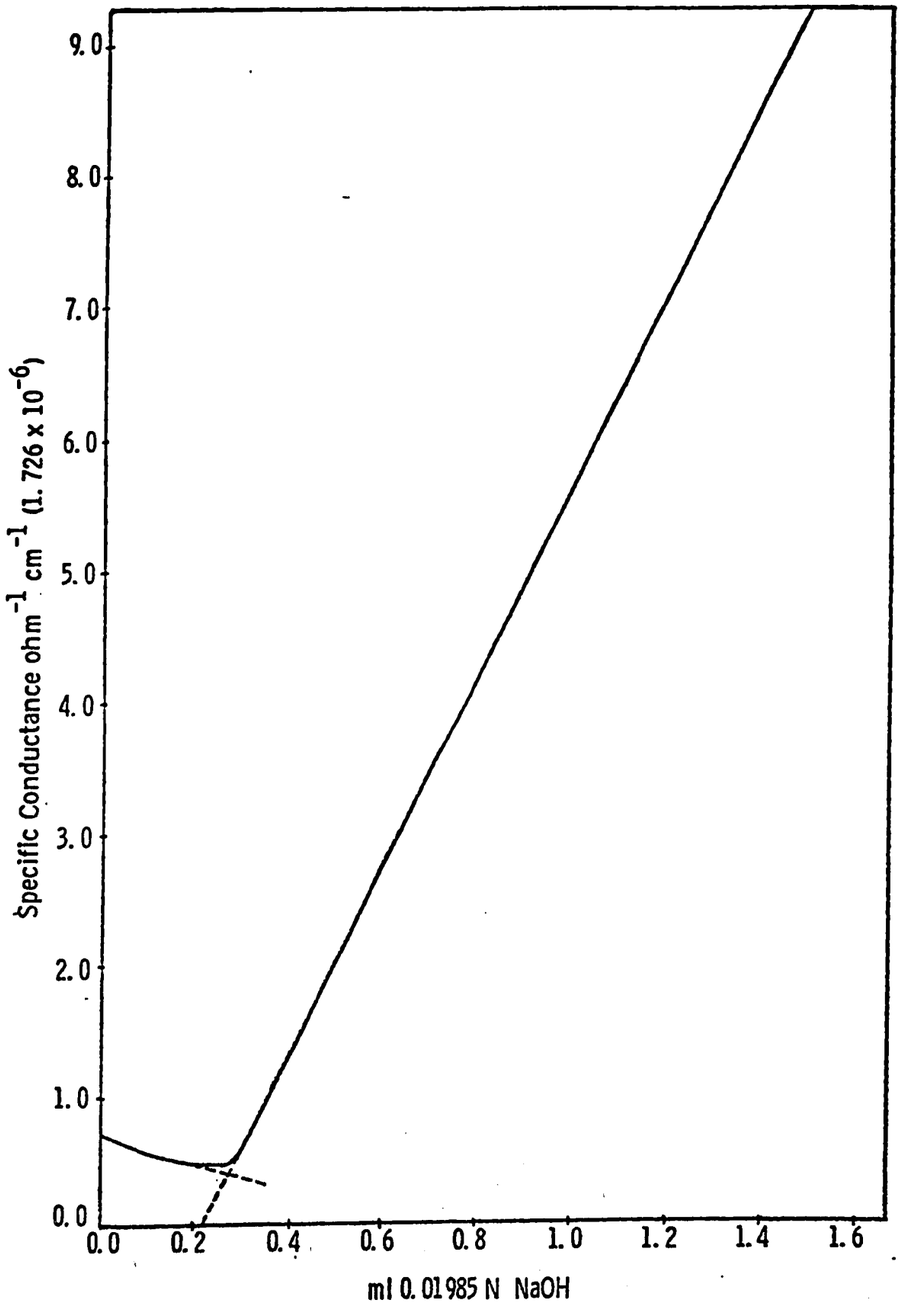


Fig. 3. Conductometric titration of cleaned Latex 1.

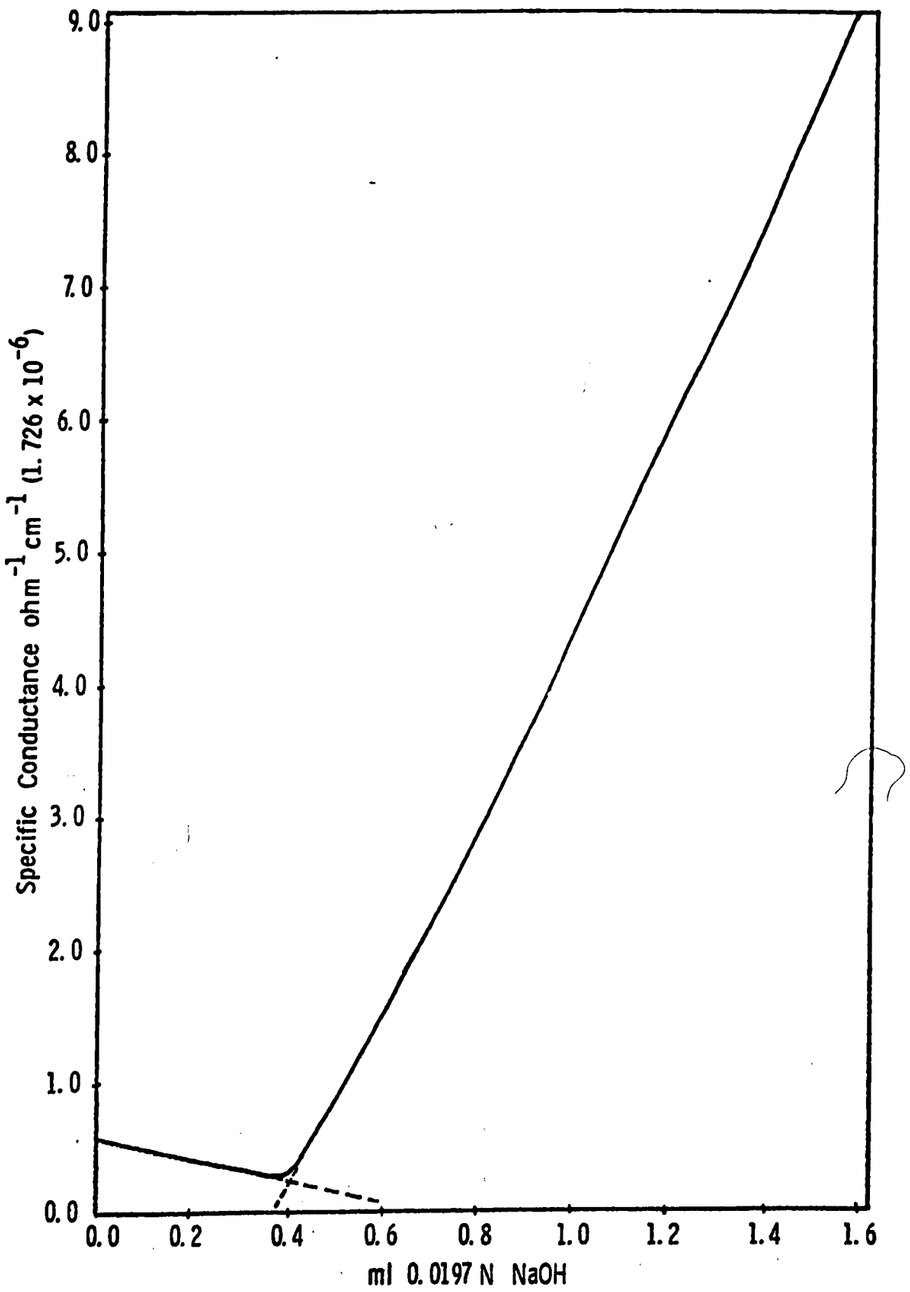


Fig. 4. Conductometric titration of cleaned Latex 2.

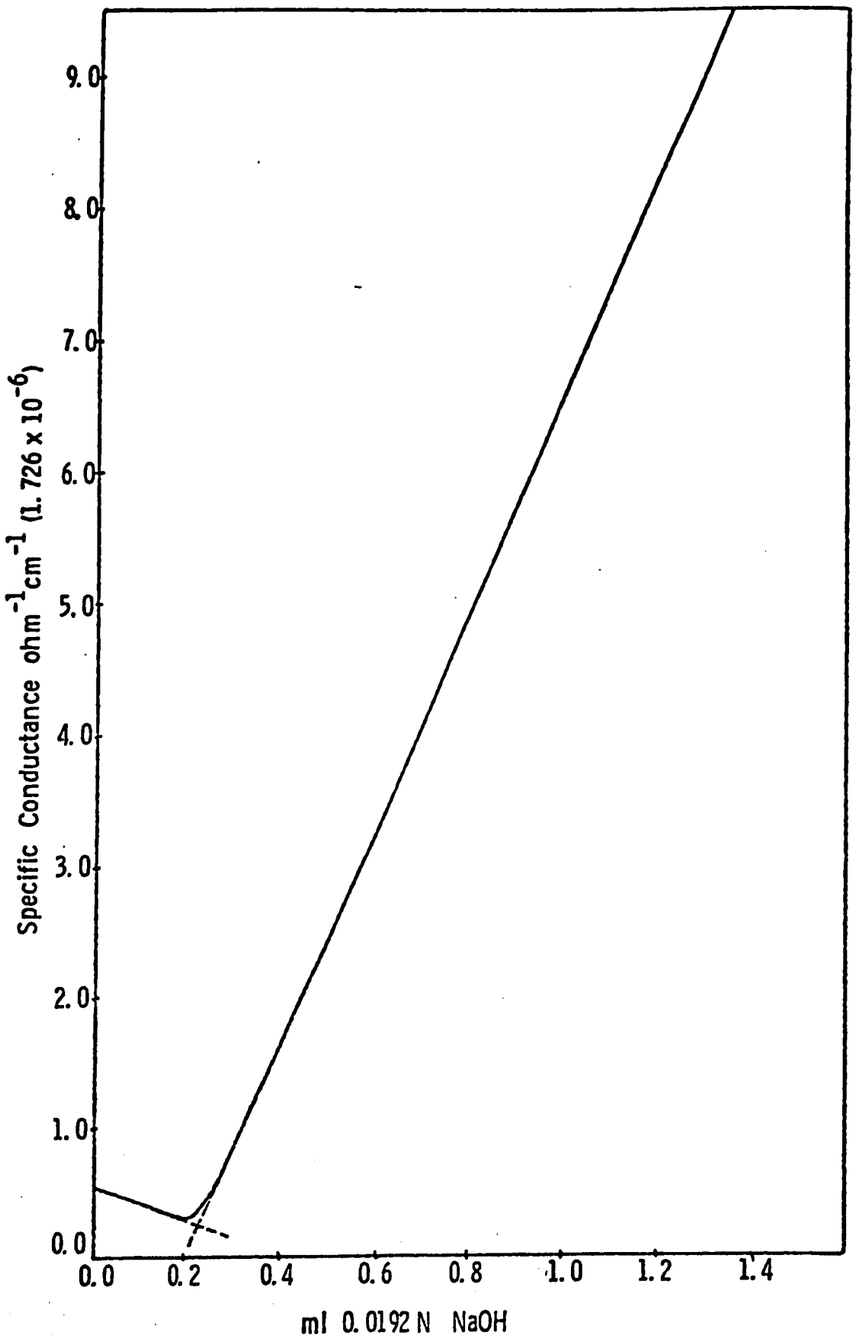


Fig. 5. Conductometric titration of cleaned Latex 3.

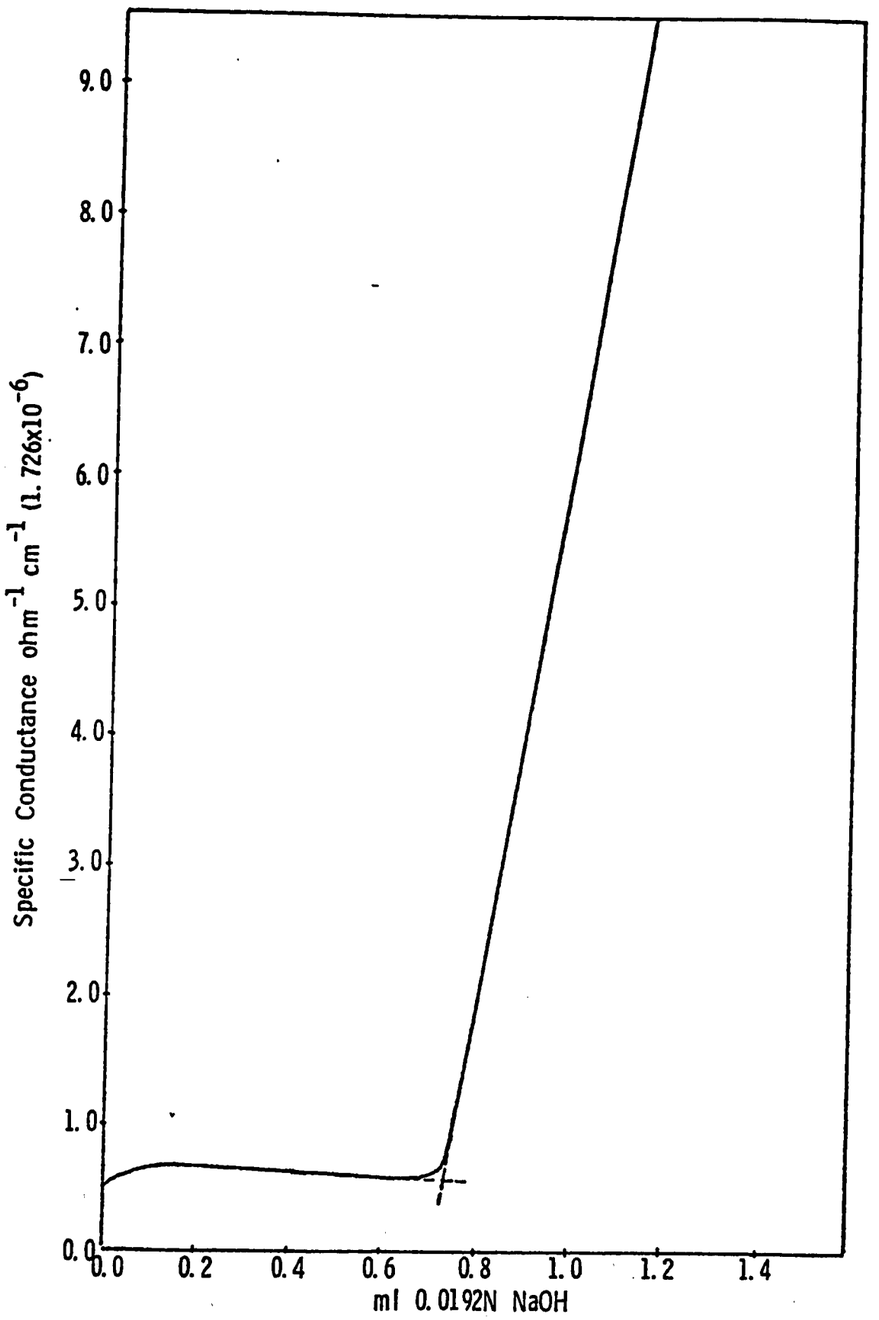
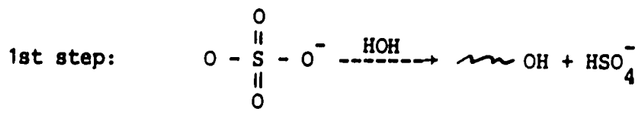


Fig. 6. Conductometric titration of cleaned Latex 4.

to hydroxyl groups and the second step is the oxidation of hydroxyl groups to carboxyl ones.

1st step:



2nd step:

The oxidized samples were cooled, subjected to dialysis, ion exchange and titration. This cycle of ion exchange and titration was repeated until a constant surface charge was obtained.

Figures 7-10 show the titration curves of the oxidized latexes. These curves show both strong and weak acidic endpoints.

These latexes behaved differently during oxidation. In many cases, increased amounts of oxidizing agent resulted in irreversible flocculation of latexes during the six-hour heating period. Different techniques were used for oxidation with each latex and this is discussed below.

Latex 1. Oxidation was tried using 0.1 gm $K_2S_2O_8$ per gram polymer but the experiment failed because of flocculation during the heating period. Aerosol MA was used to stabilize the latex during oxidation and the oxidation experiment was carried out without flocculation. The titration curve of this oxidized latex (shown in Figure 7) showed two endpoints, however. The number of sulfate endgroups was greater than in the original latex. The possible reasons for this strang result are discussed in "Results and Discussion" section.

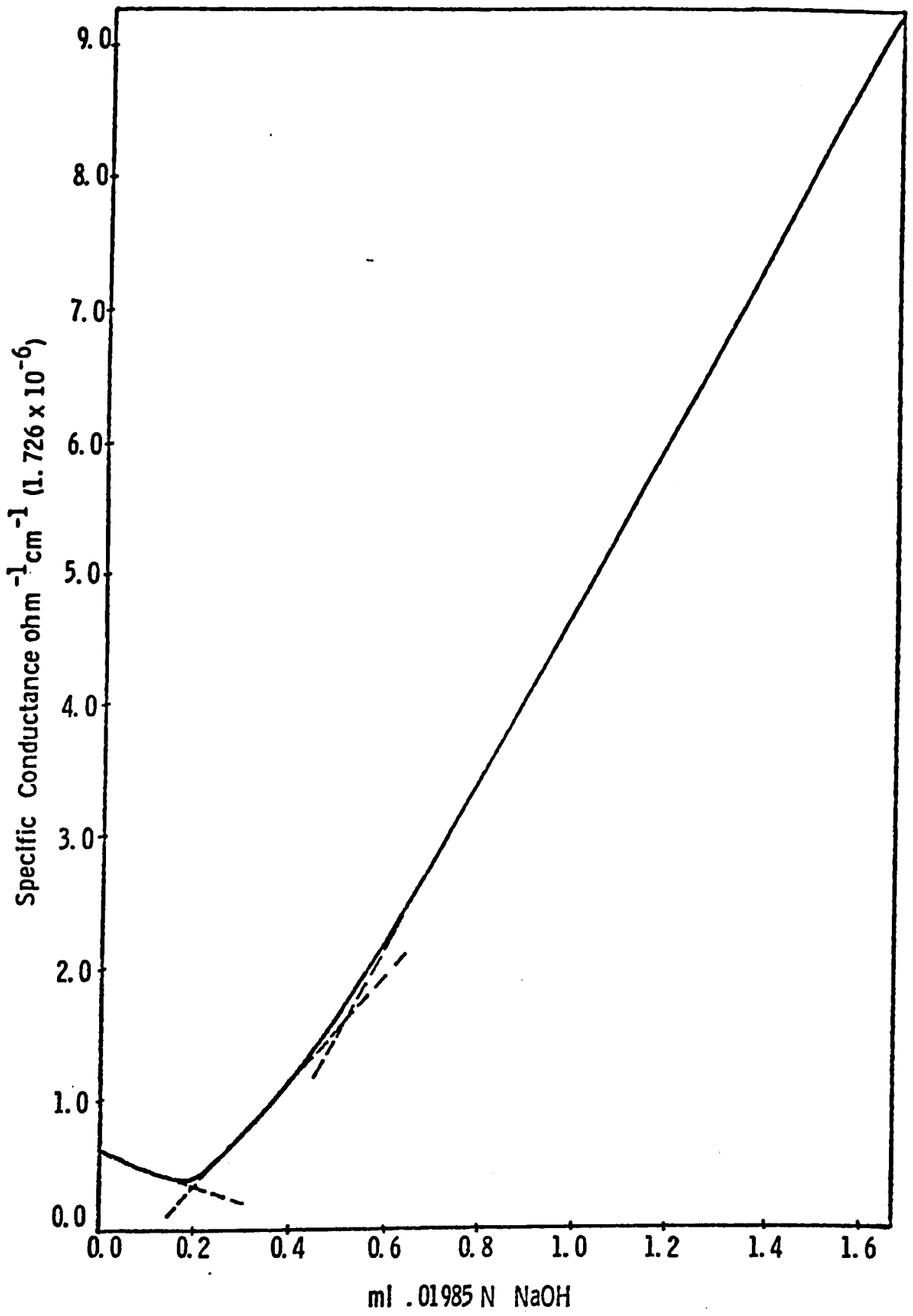


Fig. 7a. Conductometric titration of cleaned oxidized Latex 1.

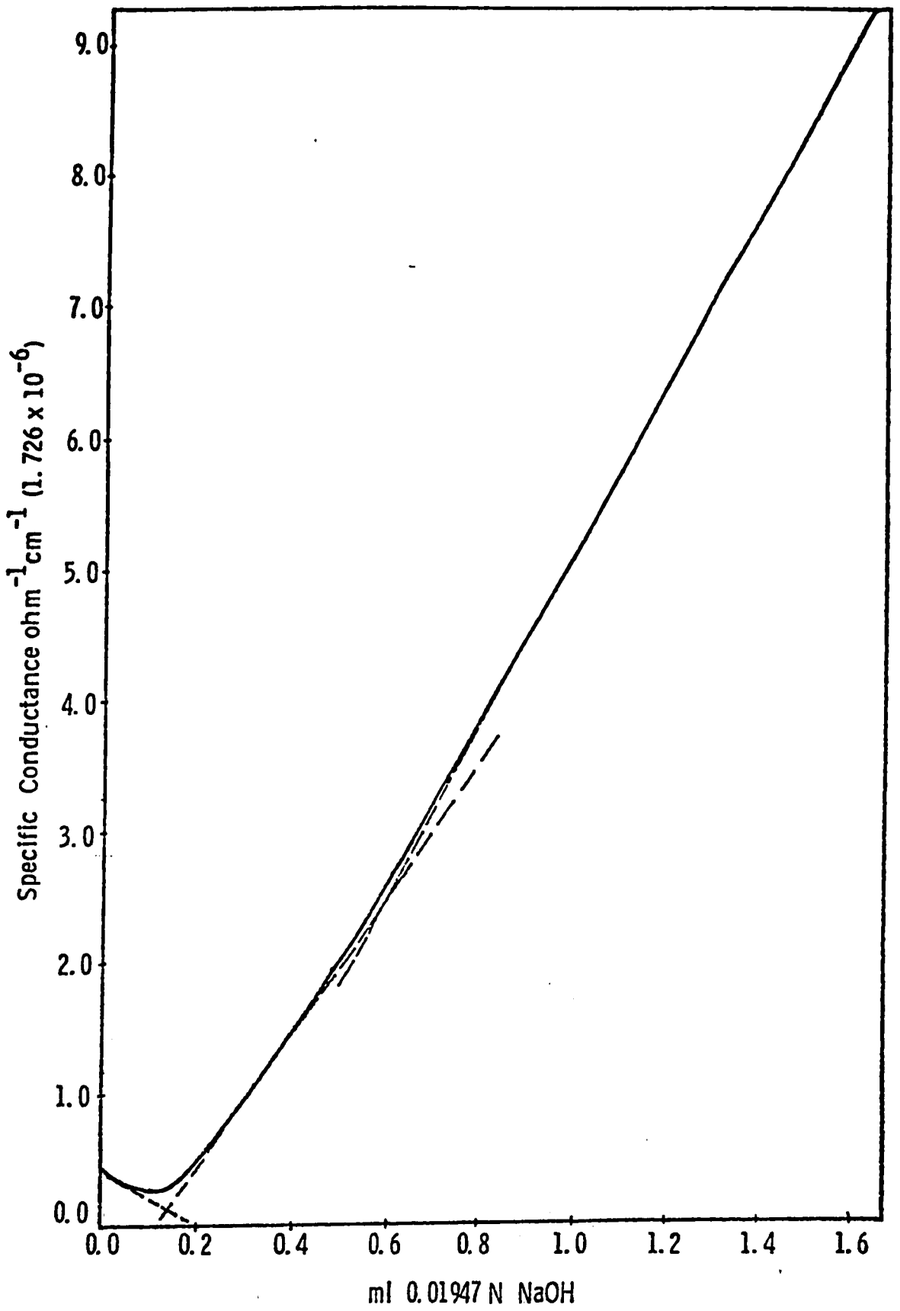


Fig. 7b. Conductometric titration of cleaned oxidized Latex 1.

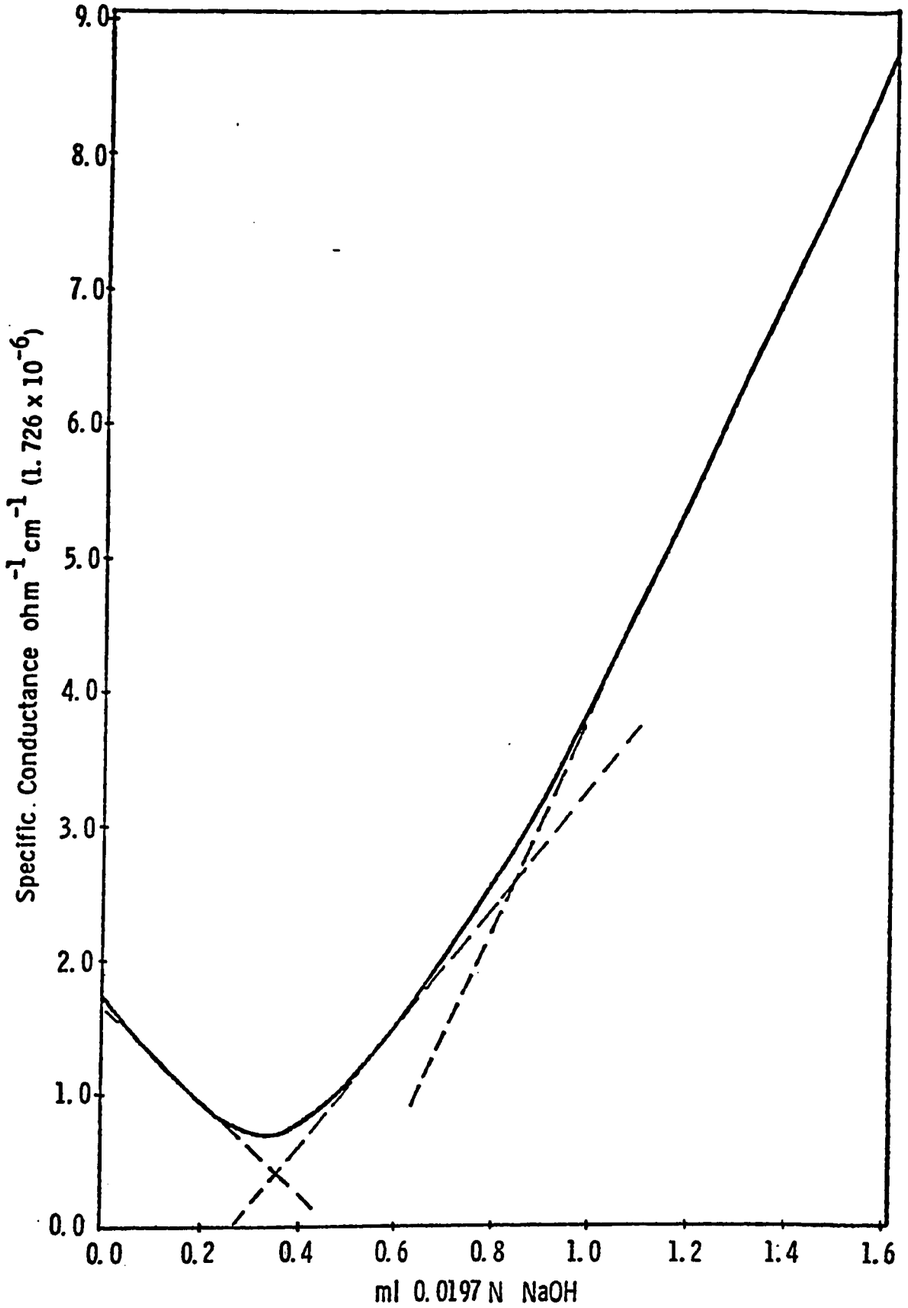


Fig. 8a. Conductometric titration of cleaned oxidized Latex 2.

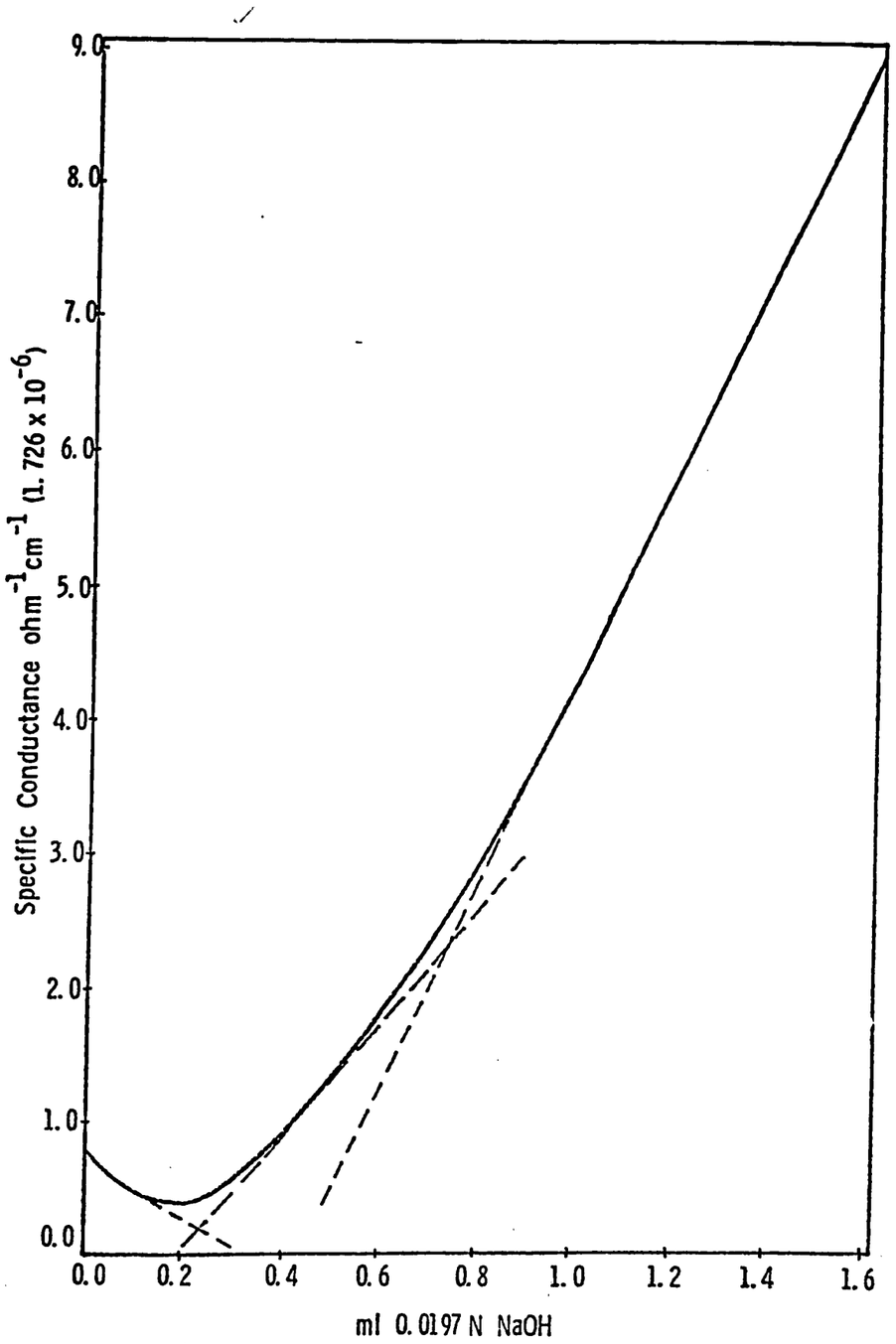


Fig. 8b. Conductometric titration of cleaned oxidized Latex 2.

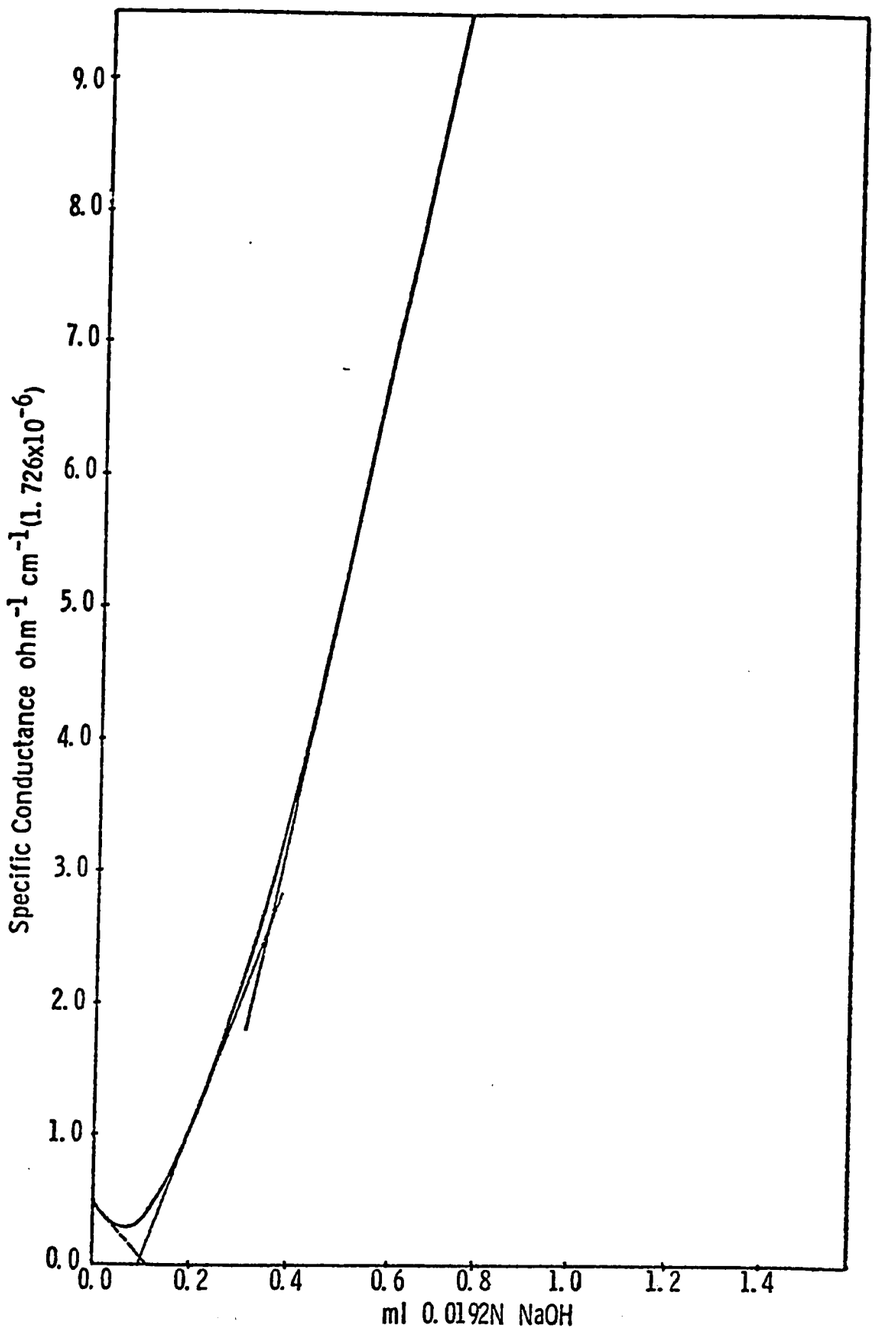


Fig. 9. Conductometric titration of cleaned oxidized Latex 3.

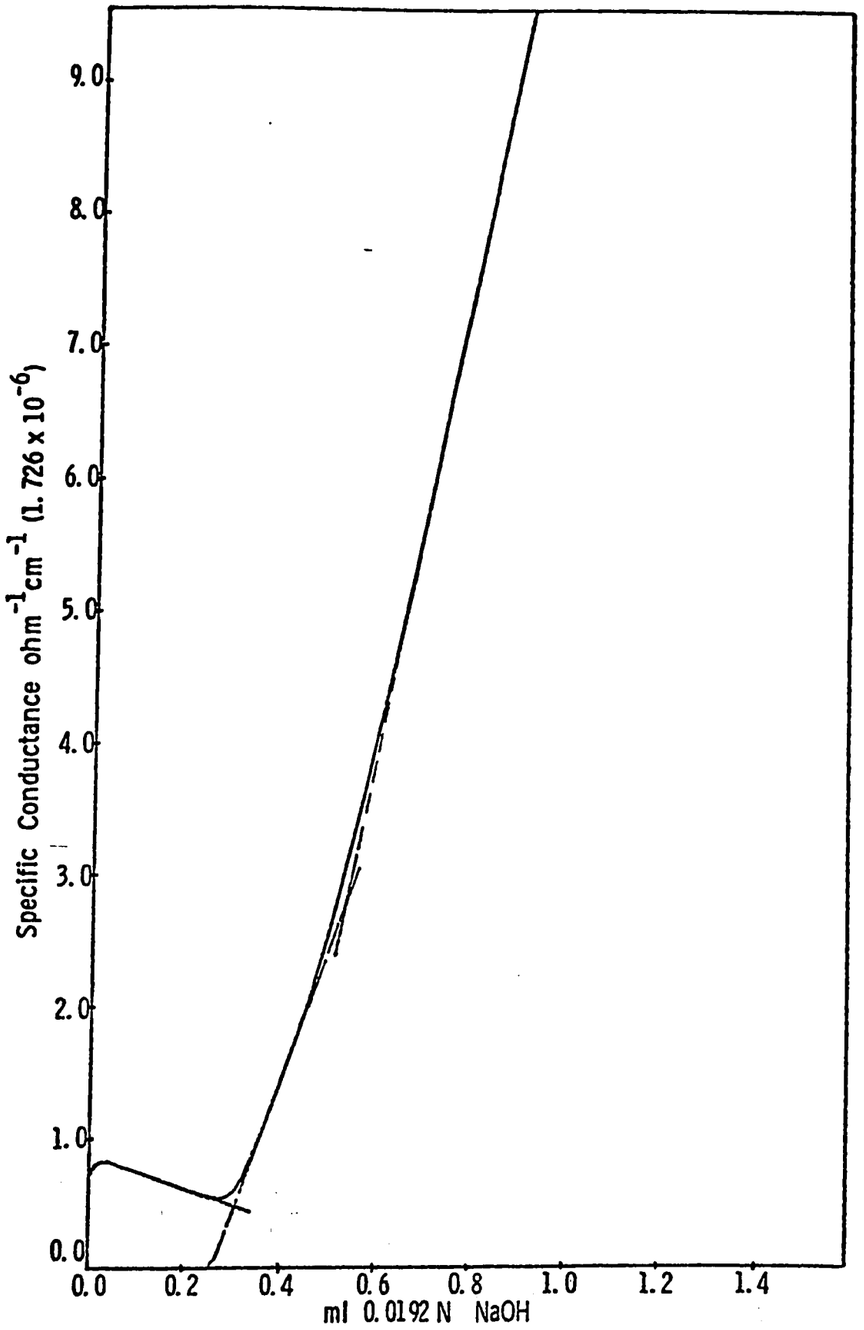


Fig. 10a. Conductometric titration of cleaned oxidized Latex 4.

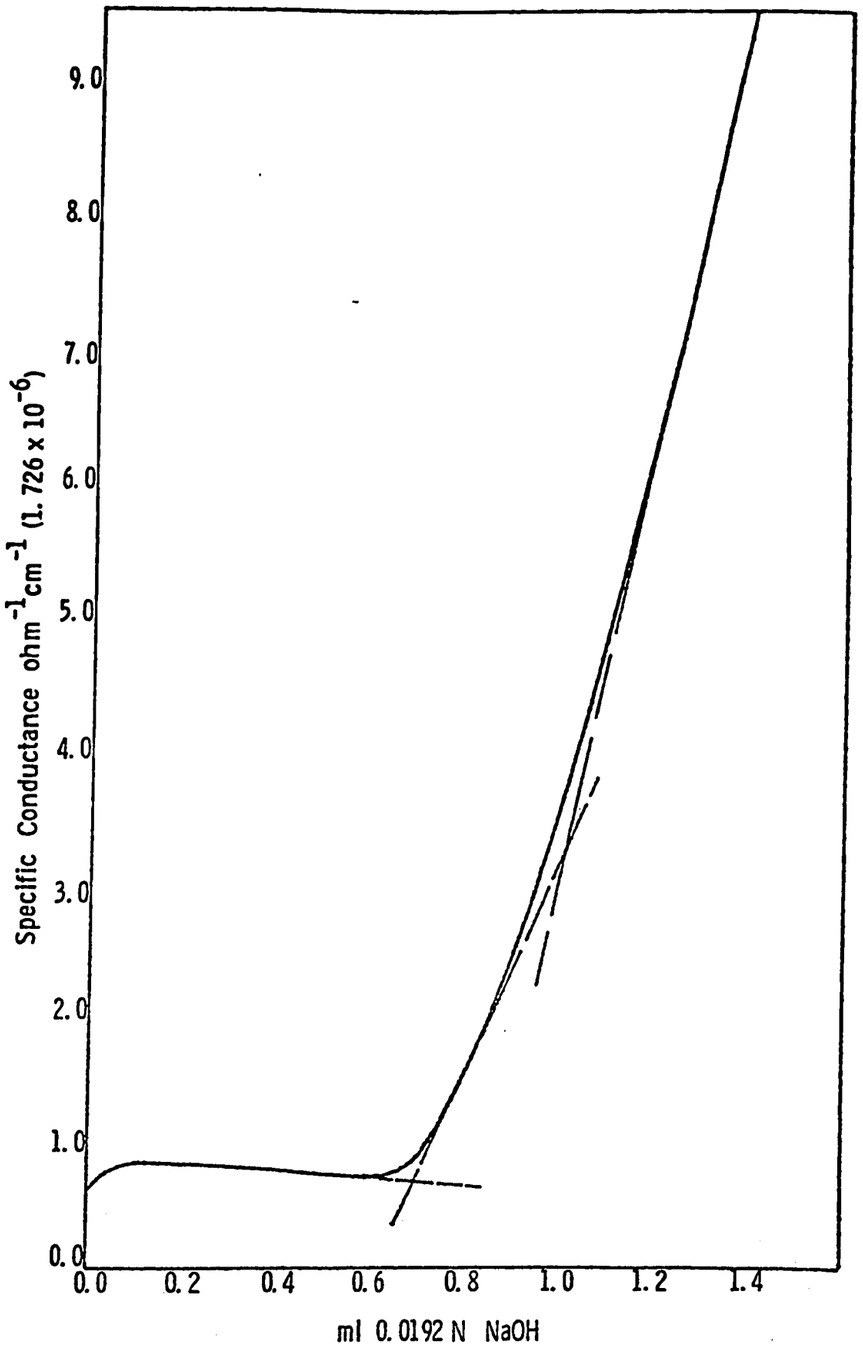


Fig. 10b. Conductometric titration of cleaned oxidized Latex 4.

Latex 2. Oxidation was started with 0.3 gms of $K_2S_2O_8$ per gram of polymer, but the latex flocculated during the reaction while it was being heated. Decreased amount of persulfate (0.1 gm/gm polymer) helped in the successful oxidation of sulfate groups. However, only a small proportion of the sulfate groups were oxidized to carboxyl groups. This oxidized latex was subjected to another step of oxidation with 0.1 gm of $K_2S_2O_8$ per gram polymer and oxidation was carried out successfully in the second step. Figure 8a shows the titration curve for the oxidized latex after the first step of oxidation and Figure 8b is the titration curve for the oxidized latex after the second step of oxidation. It is seen from the curve that even after the second step, the sulfate groups were not oxidized completely. A third oxidation step failed, resulting in a destabilized latex.

Latex 3. This latex also gave the problem of instability during oxidation; however, the use of a very diluted latex worked well. Latex having about 1% solids was oxidized with 0.1, 0.15, and 0.2 grams of $K_2S_2O_8$ per gram of polymer. The titration curve of this oxidized latex (shown in Figure 9) shows two endpoints; however, the sulfate endgroups were not oxidized completely. Increased amounts of $K_2S_2O_8$ did not help in further oxidation.

Latex 4. This latex did not give the stability problem up to 0.2 gm $K_2S_2O_8$ per gram polymer and oxidation was successful in decreasing the amount of sulfate groups. However,the oxidation of the sulfate groups could not be achieved completely. The titration curve of this oxidized latex (Figure 10) shows two endpoints.

Rheological Studies

Preliminary rheological studies were made. Viscosity-shear rate measurements were obtained with a Brookfield viscometer with U.L. adaptor, which consists of a cylinder and spindle, discussed in detail in the following section. Shear rate was varied from about 0.4 to 80 sec^{-1}. All the latex samples prepared above contained 4 to 6% solids. All the rheological studies were carried out with latexes having 4.0 ± 0.2% solids. Viscosity-shear rate data for the original latex samples and similar data after cleaning and after oxidation were obtained at 25°C.

V. APPARATUS

Conductometric Titrations

The apparatus used for conductometric titration is shown in Figure 11. Parts lists of the apparatus are as follows:

(1) Recorder (Corning Recorder 845)

(2) Fisher Accumet Model 230 pH/Ion Meter

(3) Sargent Welch Automatic Burette Model C

(4) Titrant Solution (~0.02N NaOH)

(5) Stand

(6) Conductivity Amplifier

(7) Pair of Platinum Electrode Leaf Type (Thomas Cat. #4096-D50)

(8) Magnetic Bar

(9) Jacket Cell, through which the constant temperature water circulates

(10) Standard Combination Electrode (Fisher Cat. #13-639-90)

(11) Automatic Temperature Compensator (Fisher Cat. #13-636-17)

(12) Stand

(13) Jack

(14) Powerstat Variable

(15) Haaka NB 22 Temperature Circulator ($\pm$ 0.1^{o}C)

(16) Magnetic Stirrer

Recorder (1) is a Corning Recorder Model 845 with dual pens, 100 mv range, 6 range module (1, 2-5, 5, 10, 50, 100 mv), 20 chart speeds without integrator.

Sargent Welch Automatic Burette (3) is a synchronous motor-driven precision-ground glass plunger moving in a glass burette barrel and dis-

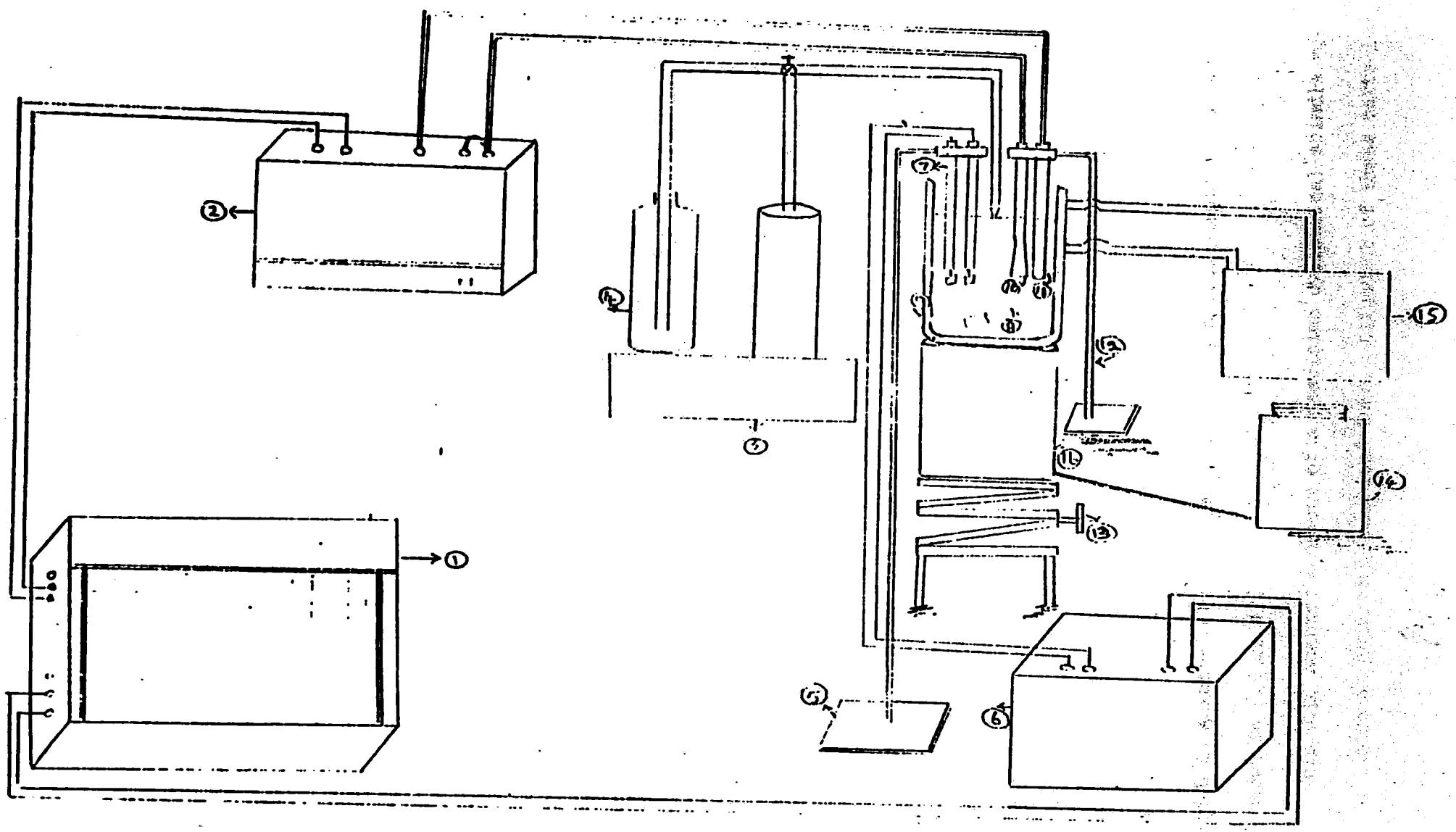


Fig. 11. Apparatus for continuous conductometric titration.

placing a volume of titrant to its effective inserted length, together with delivery, refilling and flushing facilities. The synchronous drive provided produces delivery rates of 0.8 ml/min., 0.4 ml/min., 0.16 ml/min. and 0.08 ml/min. The rate of 0.8 ml/min. was used during most of the experiments.

The conductivity amplifier (6) is an amplifier made by Mr. C. L. Cronan, a chemistry graduate student at Lehigh University. It consists of a constant voltage power supply, a transformer, a full-wave rectifier, a filter capacitor, an operational amplifier and resistors. The current flowing through the cell is rectified to D.C., filtered and allowed to pass through one of the several resistors and the voltage drop across these resistors is amplified and sent to the recorder.

Oxidation

The oxidation reactions were carried out in bottles which were heated in a tumbling constant temperature water bath. Bottles were placed in a cage with six compartments which tumble at 26 RPM speed.

Viscosity Measurements

Viscosity measurements were made with a Brookfield model LV synchrolectric viscometer. Viscosity measurements of low viscosity materials can be done on this instrument with good precision with the Brookfield U.L. Adaptor. Brookfield viscometer and U.L. Adaptor arrangement are shown in Figure 12.

This U.L. Adaptor consists of a precision cylindrical spindle rotating inside an accurately machined tube. Alignment of these parts is

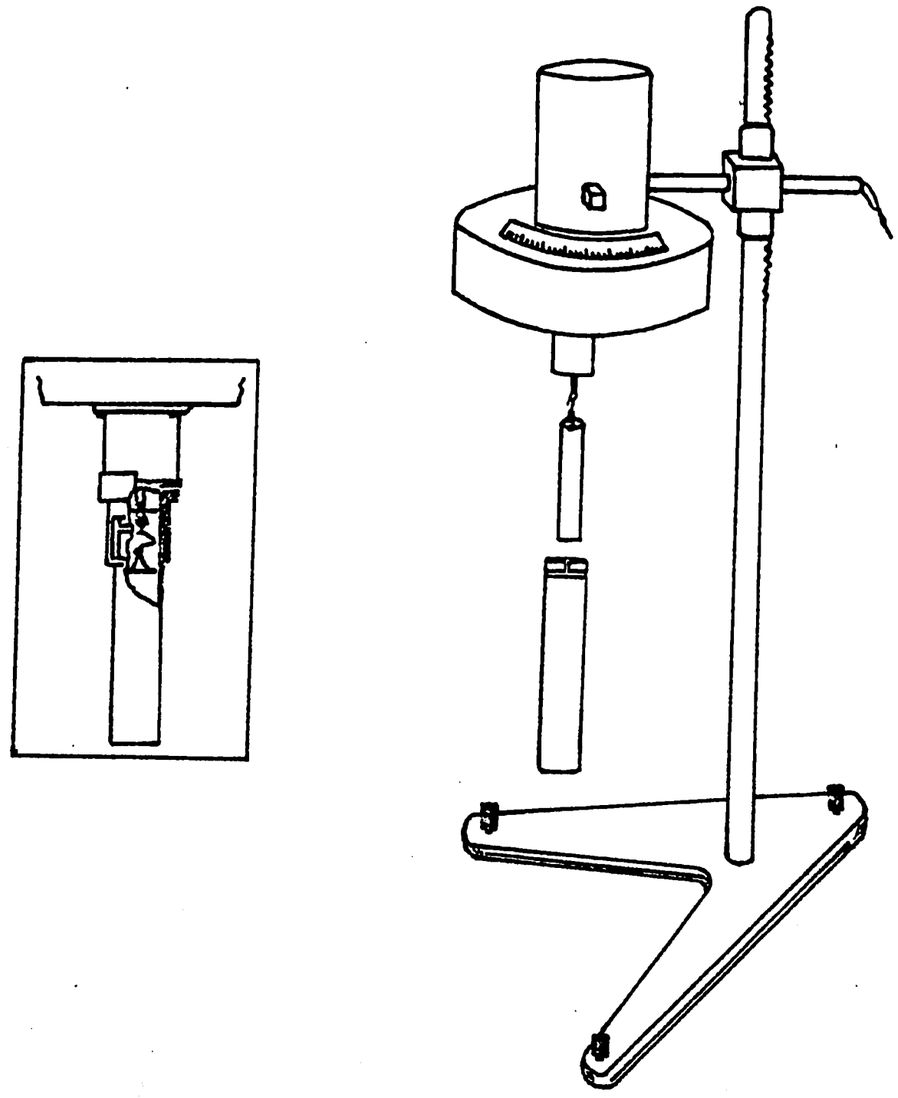


Fig. 12. Brookfield Viscometer with U.L. Adopter

accomplished by a special pivot housing and adaptor body. Two tubes are furnished with each adaptor. One has an open end for measurements in tanks or beakers. Another one is the closed tube which holds 20 cc of sample and can be immersed in a temperature bath.

The viscometer should be leveled during its operation. The instrument was calibrated using standard Newtonian fluids. The spindle and the tube were washed with distilled deionized water before use.

The Brookfield viscometer is simple to operate. The spindle speed is set and the torque reading of the instrument is recorded and multiplied by a conversion factor to give the viscosity in centipoises. Shear rates were calculated by the consideration of the spindle and tube geometry.

VI. RESULTS AND DISCUSSION

Table 2 shows the results of ion exchange cycles on the polystyrene latex of 190 nm diameter (Latex #1). The surface charge increased for the first three cycles, then decreased and became constant after six cycles. It reached a shallow maximum after the third cycle. The increase may be due to incomplete exchange between hydrogen ions of the resin and potassium and sodium cations of the latex. The constancy of the charge even after more cycles indicated that these charges are an integral part of the polymer.

Figures 3-6 (page 27-30) show the conductometric titration curves for the original polystyrene and the styrene-butadiene copolymer latexes after cleaning by ion-exchange method. There was only one endpoint on curves 3, 5, and 6 and these were strong acidic endpoints. Curve 4 shows a slight change in the slope after the strong acidic endpoint. This may be due to dissolved carbon dioxide. Presumably the latexes under investigation had only sulfate endgroups at the particle surface. These results match with the results obtained by Vanderhoff and his coworkers (19,26,27). These latexes were prepared with persulfate initiator. The decomposion of this initiator is as follows:

$$S_2O_8^{-2} \longrightarrow 2SO_4^{-}$$

The sulfate ion-radicals react with the monomer, which is present in small quantities in the aqueous phase as follows:

TABLE 2.

Results of ion exchange of polystyrene latex of 190 nm diameter.

Ion Exchange Cycle	$\frac{\mu \text{ moles } SO_4^-}{\text{gram polymer}}$	$\frac{\mu C}{cm^2}$
1st	.83	0.91
2nd	4.82	1.55
3rd	4.79	1.60
4th	4.63	1.49
5th	4.57	1.47
6th	4.56	1.46
7th	4.56	1.46

$$SO_4^{-}\cdot + M \longrightarrow SO_4^{-}M\cdot$$

$$SO_4^{-}M\cdot + M \longrightarrow SO_4^{-}MM\cdot$$

when the oligomers grow in monomer units up to 4, 5, or 6 and become surface-active and then migrate to an oil-water interface and are adsorbed with the radical end oriented toward the hydrophobic phase and polymerization continues within the particle or at the particle surface until the termination takes place by entry of second radical.

There should be two sulfate endgroups for each polymer molecule and these polymer endgroups should be on the latex particle surface provided:

(1) the sulfate ion radical does not undergo a transfer reaction,

(2) none of the sulfate endgroups are buried within the particle,

(3) termination within the particle occurs by combination.

This value of two endgroups per molecule on the surface may be lower if some sulfate endgroups were buried within the particle and thus undetected by conductometric titration. One other reason would be the termination process, that is, if the termination occurs by disproportionation. In addition, the sulfate radicals may produce hydroxyl radicals and these hydroxyl radicals may initiate polymerization. The production of hydroxyl groups is suggested by Kolthoff and Miller (32) by the following reactions:

$$SO_4^{-}\cdot + H_2O \longrightarrow HO\cdot + HSO_4^{-}$$

The presence of these hydroxyl groups cannot be determined by titration. The latexes under investigation had hydroxyl groups as is discussed later in this report.

Figures 7-10 (pages 32-38) are the conductometric titration curves for the latexes 1-4 after oxidation, respectively. All these curves show two endpoints. One is for strong acid groups, and another one for weak acid. We believe that after oxidation, these samples had sulfate as well as carboxylic groups on their surfaces. Tables 3-6 show the results of oxidation of sulfate and hydroxyl endgroups of latexes 1-4, respectively.

Results of the oxidation of latex 1 were quite strange. There was an increase in the number of strong acid groups at the particle surface, and there were some weak acidic groups also at the particle surface. This increase in the number of sulfate groups was thought to be due to one of the following reasons:

(1) The "Aerosol MA" used to stabilize the latex during oxidation was not completely removed from the surface by ion exchange. An experiment was done with freshly cleaned latex. The surface charge was measured, then a known amount of Aerosol MA was added and the added emulsifier, Aerosol MA, was desorbed completely by ion exchange. The surface charge became constant at the same value which was measured for the original clean latex. So this possibility was ruled out.

(2) The "Aerosol MA" used to stabilize the latex during oxidation might have undergone a transfer reaction and became an integral part of the latex. Another experiment was carried out to test this hypothesis. The freshly cleaned latex was stabilized with a fluorocarbon surfactant, ZONAL FSA, from E. I. duPont de Nemours and Co. This surfactant should not undergo a transfer reaction. The conductometric titration curve for this oxidized latex is shown in

TABLE 3.

Results of hydrolysis and oxidation of sulfate and hydroxyl endgroups of

Latex #1 - 190 nm diameter polystyrene latex

Hydrolysis was carried out under acid and basic conditions at room temperature and at 70°C.

Oxidation was carried out using 0.1 gm $K_2S_2O_8$ per gram polymer and 10^{-5}M $AgNO_3$ at 90°C.

Latex	$\frac{\mu \text{ moles } SO_4}{\text{gram polymer}}$	$\frac{\mu \text{ moles COOH}}{\text{gram polymer}}$	$\frac{\mu \text{ moles OH}}{\text{gram polymer}}$
Before oxidation	4.5	0.0	---
Acid hydrolysis	5.6	0.0	---
Basic hydrolysis	4.8	0.0	---
Oxidized Latex (1)	5.8	8.9	8.9
Oxidized Latex (2)	6.2	10.9	10.9

TABLE 4

Results of oxidation of sulfate and hydroxyl endgroups of

Latex #2 - 210 nm diameter styrene-butadiene copolymer latex

Successive oxidation was carried out using 0.1 g of $K_2S_2O_8$ per gram of olymer and 10^{-5}M $AgNO_3$ at 90°C.

Latex	$\frac{\mu \text{ moles } SO_4}{\text{gram polymer}}$	$\frac{\mu \text{ moles COOH}}{\text{gram polymer}}$	$\frac{\mu \text{ moles OH}}{\text{gram polymer}}$
Before oxidation	9.0	0.0	---
After first oxidation	6.2	8.8	6.0
After second oxidation	5.5	11.5	8.0

TABLE 5.

Results of oxidation of sulfate and hydroxyl endgroups of

Latex #3 - 300 nm diameter polystyrene latex.

Oxidation was carried out at very low concentration of polymer in latex, using 0.15 gm $K_2S_2O_8$/gram polymer and 10^{-5}M $AgNO_3$ at 90°C.

Latex	$\frac{\mu \text{ moles } SO_4}{\text{gram polymer}}$	$\frac{\mu \text{ moles COOH}}{\text{gram polymer}}$	$\frac{\mu \text{ moles OH}}{\text{gram polymer}}$
Before oxidation	5.4	0.00	---
Oxidized latex	4.8	12.2	11.6

TABLE 6.

Results of oxidation of sulfate and hydroxyl endgroups of

Latex #4 - 576 nm diameter polystyrene latex.

Oxidation was carried out using 0.15 gram $K_2S_2O_8$ per gram polymer and 10^{-5}M $AgNO_3$ at 90°C.

Latex	$\frac{\mu \text{ moles } SO_4}{\text{gram polymer}}$	$\frac{\mu \text{ moles COOH}}{\text{gram polymer}}$	$\frac{\mu \text{ moles OH}}{\text{gram polymer}}$
Before oxidation	7.7	0.00	---
Oxidation (1)	7.5	3.3	3.1
Oxidation (2)	6.5	4.7	3.5

Figure 7b (page 33). This curve also shows two endpoints, one for strong acid and another one for weak acid. Again the number of sulfate groups was more than what was there in the original latex and, thus, this possibility was not correct.

(3) Hydrolysis of sulfate groups to hydroxyl groups was possible, but doubtful.

Two separate experiments were done to check the hydrolysis. Freshly cleaned latex samples were placed in bottles and heated at 70°C for about 12 hours at a pH of 2 (H_2SO_4 was used to adjust the pH). The conductometric titration curves for these hydrolyzed latexes are shown in Figures 13 and 14. The curve in Figure 13 shows one endpoint for the strong acid group and there was a slight change in the slope which may be an indication of a weak acid. The curve in Figure 14 shows only one endpoint. The amount of sulfate endgroups was slightly more than what was there in the original latex. These experimental results suggest that hydrolysis was not taking place at all. Two other hydrolysis experiments were carried out at room temperature without any change in the number of sulfate groups. The results were approximately the same as those of the original clean latex. This failure of hydrolysis caused us to think about the nature of the strong acidic groups. Since the sulfate groups are easily hydrolyzable the other strong acidic groups, which were not easily hydrolyzed, would be sulfonate endgroups. Conductometric titration techniques cannot be used to distinguish between these two groups. Figures 15 and 16 are conductometric titration curves for sulfonate and sulfate emulsifiers, respectively. Figure 15 shows the conductometric titration curve of

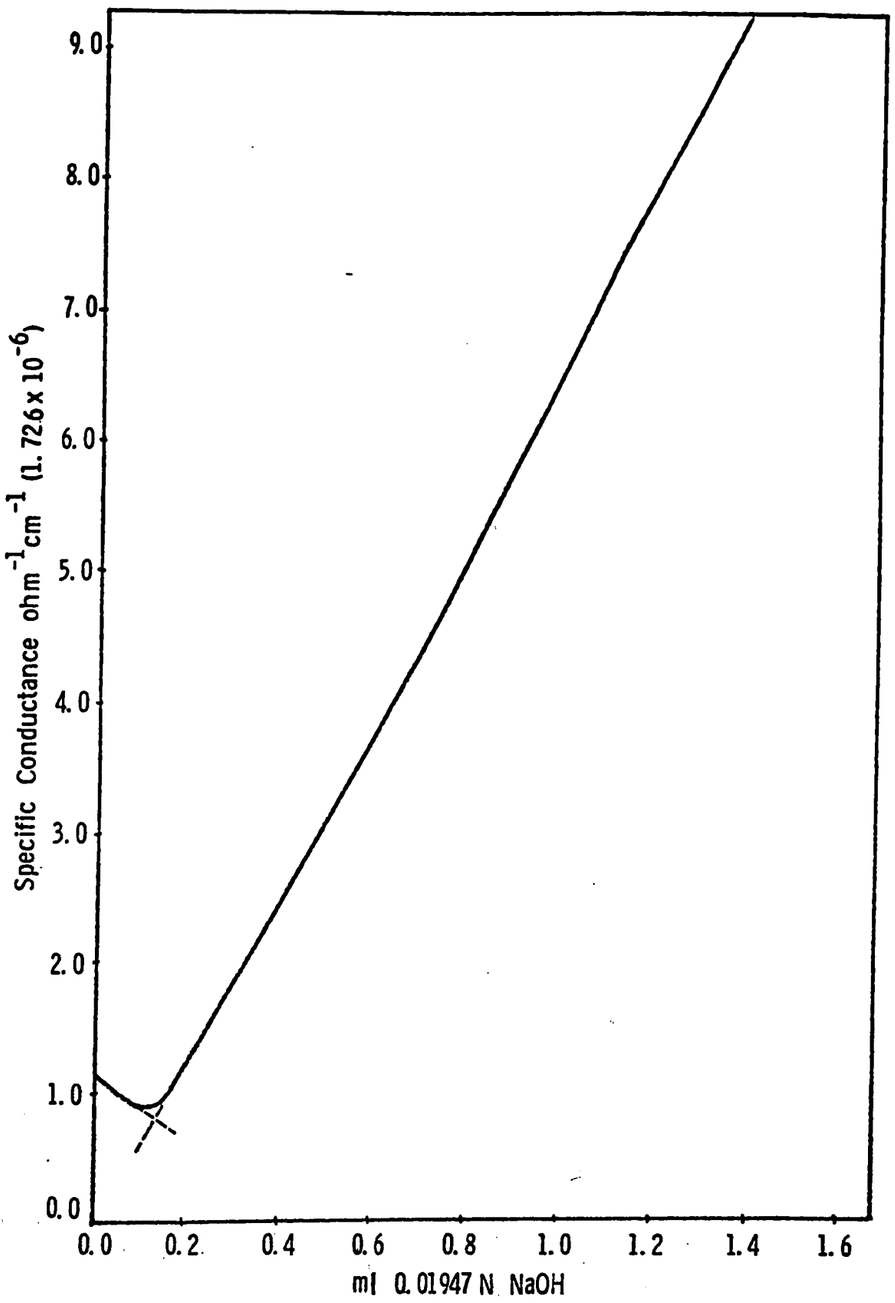


Fig. 13. Conductometric titration of cleaned Latex 1. after acid hydrolysis.

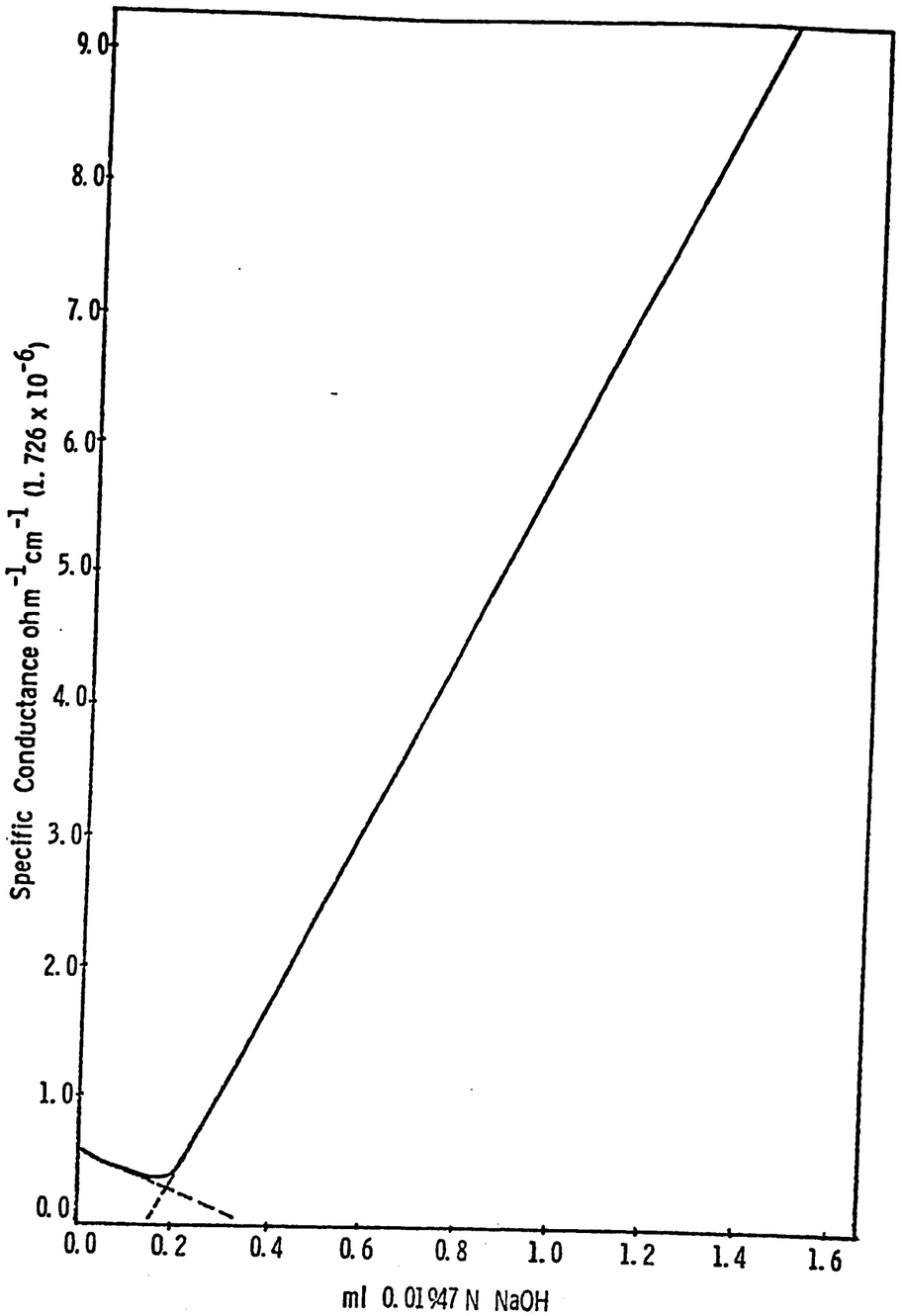


Fig. 14. Conductometric titration of cleaned Latex 1 after basic hydrolysis.

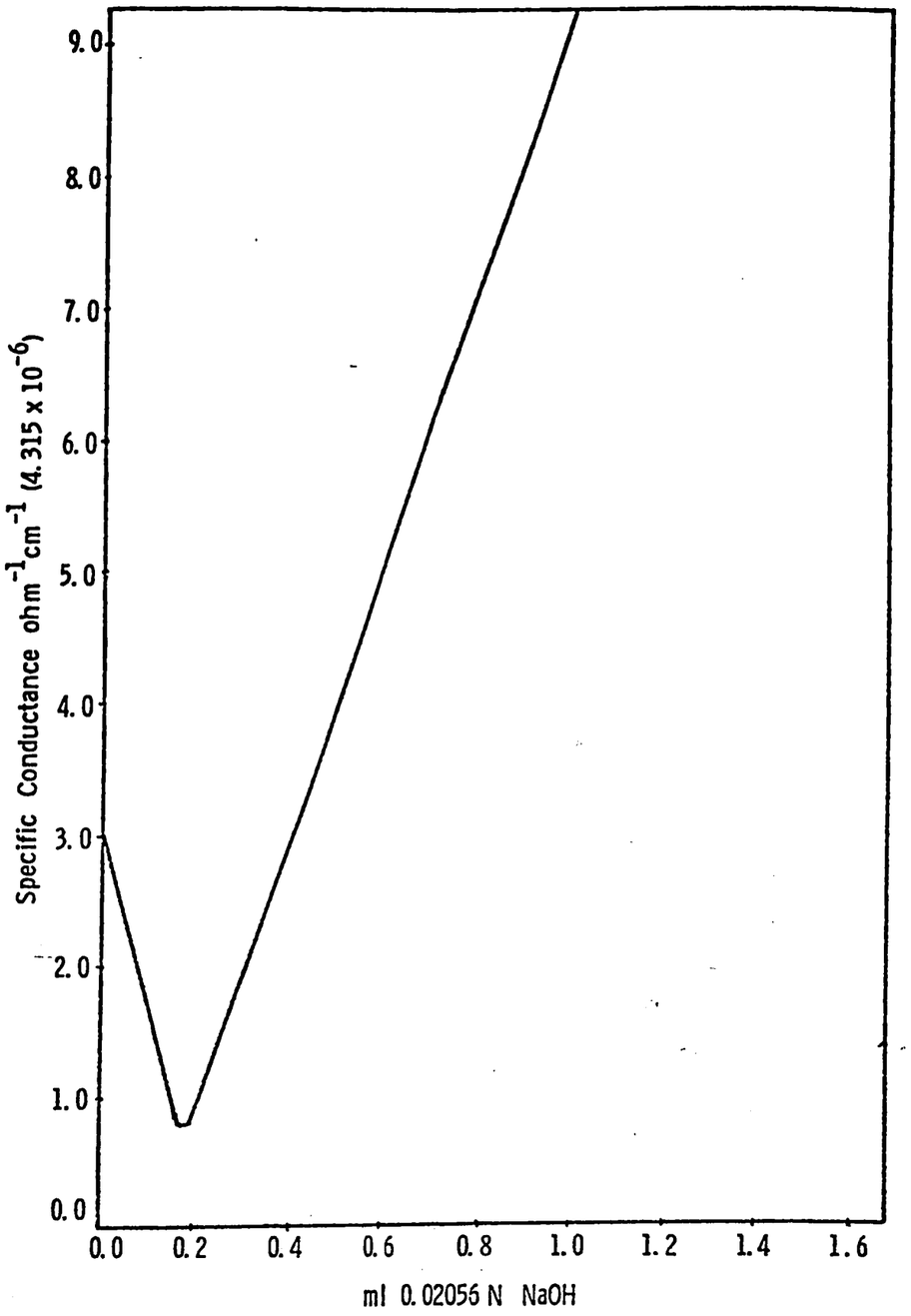


Fig. 15. Conductometric titration of ion-exchanged Aerosol MA solution.

"Aerosol MA" solution ion exchanged with Dowex 50W in the hydrogen form. Figure 16 is the conductometric titration curve of sodium lauryl sulfate ion exchanged with Dowex 50W in hydrogen form. Literature about the decomposition of $K_2S_2O_8$ shows that this dissociates to give sulfate groups and there is no evidence which would suggest the formation of sulfonate groups from $K_2S_2O_8$.

Ghosh et al. (33,34,35) developed and used dye partition and dye interaction methods to study the endgroups in polymer. They applied these techniques for the polymers prepared by bulk and solution polymerization. Dye interaction technique can be used to distinguish between sulfate and sulfonate endgroups. This experiment is suggested for further investigation and continuation of this work.

(4) One other possibility for the increase in the number of sulfate endgroups after the oxidation reaction was that some of the buried sulfate endgroups might have come up to the surface during the oxidation and hydrolysis processes or there may be some active polymer molecules in the latex, which were not terminated and during oxidation process termination of these active molecules took place and thus the sulfate endgroups increased in number. No work has been done during this research to check these possibilities.

Results of the oxidation process of other latexes showed that after oxidation, each of these latex particles have two different kinds of surface endgroups, strong and weak acid groups. This indicates that the oxidation of the sulfate endgroups was not achieved completely. The appearance of the weak acidic groups was partly due to the oxidation of these

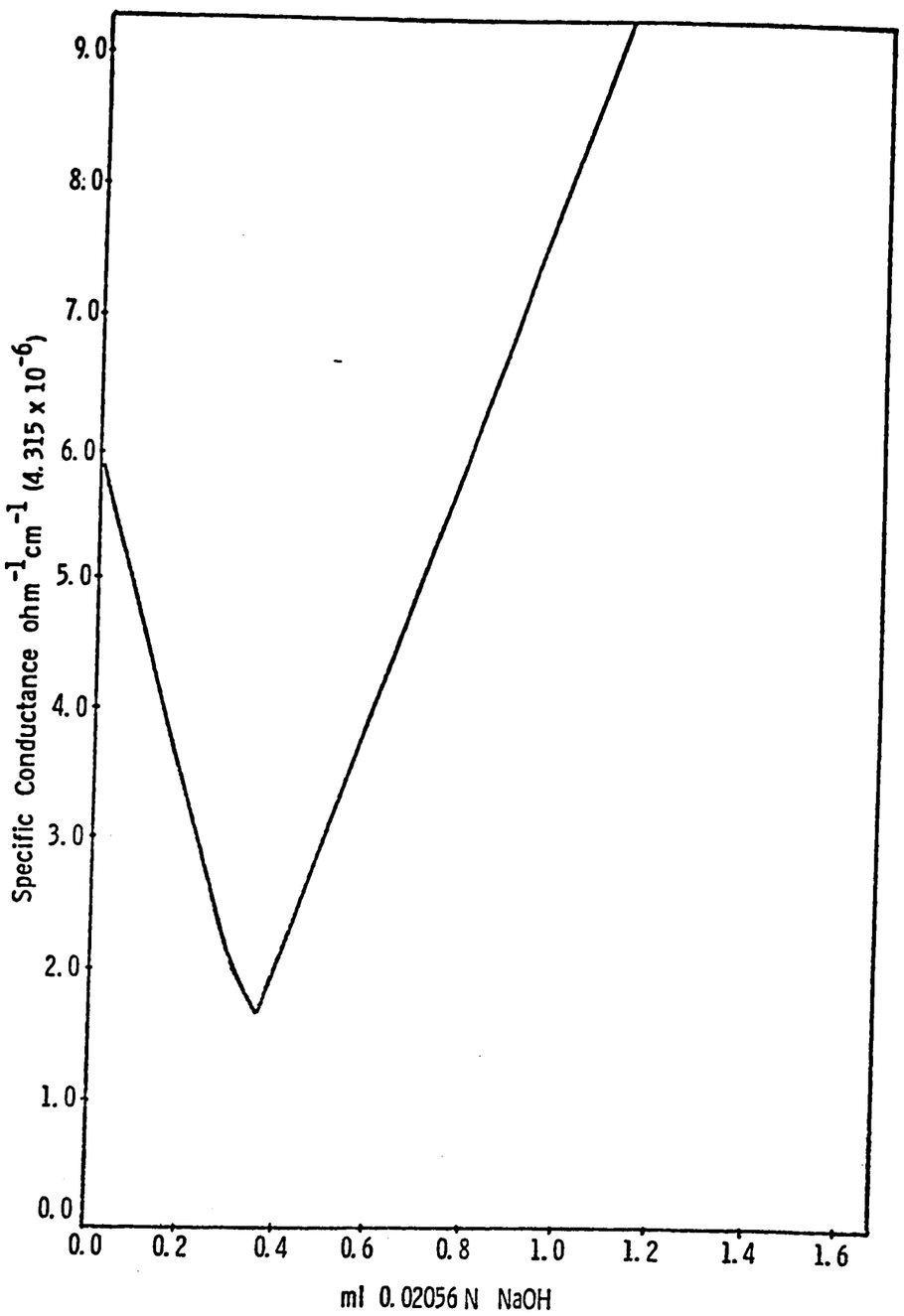


Fig. 16. Conductometric titration of ion-exchanged NaLS solution.

sulfate groups and mostly due to the oxidation of hydroxyl groups which were present at the particle surface but not detected by titration method. Oxidation is a good technique to determine the amount of hydroxyl groups at the particle surface.

From the results of oxidation processes, we can also conclude that the sulfate endgroups can be hydrolyzed and subsequently oxidized to carboxyl groups with higher amounts of oxidizing agent; however, the resulting completely carboxylated latexes were unstable.

Tables 7 and 8 show the viscosity-shear rate values for latexes 1 and 3, respectively, before and after cleaning. Tables 9 and 10 show the viscosity-shear rate values for latexes 2 and 4. Tables 9 and 10 also have the viscosity-shear rate values for the clean latex before and after oxidation when they are cleaned with Dowex 50W in Na^+ form (values in columns 4 and 6 of these tables). Table 11 summarizes the viscosities of latexes 1-4 according to particle size. These viscosity-shear rate values (reported in Tables 7 through 11) were plotted in Figures 17-22.

All the original latex samples appear to be Newtonian. On the other hand, the rheological behavior of all these samples after cleaning with ion exchange resins was strongly non-Newtonian even at very low volume fraction; however, the oxidized latexes, after cleaning, were Newtonian and had low viscosities which were very close to the uncleaned original latex viscosities.

The large increase in viscosities and the non-Newtonian behavior of the emulsifier and electrolyte-free latexes, before oxidation, was expected and presumably due to the second electroviscous effect, discussed

TABLE 7.

Viscosities* of PS Latex of 190 nm diameter

Solids: 4% Temperature: 25°C

	Shear rate sec^{-1}	Original latex	Original latex cleaned
1	0.38	---	57.00
2	1.89	1.2	29.60
3	7.55	1.2	15.40
4	38.00	1.0	5.32
5	75.50	1.15	3.77

*C.P.

TABLE 8.

Viscosities* of PS Latex of 300 nm diameter

Solids: 4% Temperature: 25°C

	Shear rate sec^{-1}	Original latex	Original latex cleaned
1	0.38	---	38.66
2	1.89	1.2	18.53
3	7.55	1.2	8.23
4	38.00	1.0	2.94
5	75.50	1.06	2.40

*C.P.

TABLE 9.

Viscosities (in c.p.) of polystyrene-butadiene copolymer latex of 210 nm diameter

Solids: 4%

Temperature: 25°C

S. No.	Shear Rate sec^{-1}	Original Latex	Original Latex Cleaned in H^+ form	Original Latex Cleaned in Na^+ form	Oxidized Latex Cleaned in H^+ form	Oxidized Latex Cleaned in Na^+ form
1	0.38	--	72.00	12.00	--	12.00
2	1.89	1.20	28.00	4.00	1.60	4.00
3	7.55	1.30	13.00	1.90	1.15	1.90
4	38.00	1.02	4.74	1.12	1.09	1.12
5	75.50	1.12	3.36	1.12	1.15	1.12

TABLE 10.

Viscosities (in c.p.) of polystyrene latex of 576 nm diameter.

Solids: 4%

Temperature: 25°C

S. No.	Shear Rate sec^{-1}	Original Latex	Original Latex Cleaned in H^+ form	Original Latex Cleaned in Na^+ form	Oxidized Latex Cleaned in H^+ form	Oxidized Latex Cleaned in Na^+ form
1	0.38	--	21.33	6.00	--	6.00
2	1.89	1.20	6.00	2.00	1.32	2.00
3	7.55	1.10	4.06	1.10	1.30	1.20
4	38.00	1.00	1.88	1.02	1.10	1.00
5	75.50	1.02	1.60	1.04	1.06	1.06

TABLE 11.

Viscosities* of clean latexes of different particle size.

Solids: 4%

Temperature: 25°C

S. No.	Rate sec^{-1}	Polystyrene Latex 190 nm dia.	Polystyrene-butadiene Copolymer Latex 210 nm dia.	Polystyrene Latex 300 nm dia.	Polystyrene Latex 576 nm dia.
1	0.38	57.00	72.00	38.66	21.33
2	1.89	29.60	28.00	18.53	6.00
3	7.55	15.40	13.00	8.23	4.06
4	38.00	5.32	4.74	2.94	1.88
5	75.50	3.77	3.36	2.40	1.60

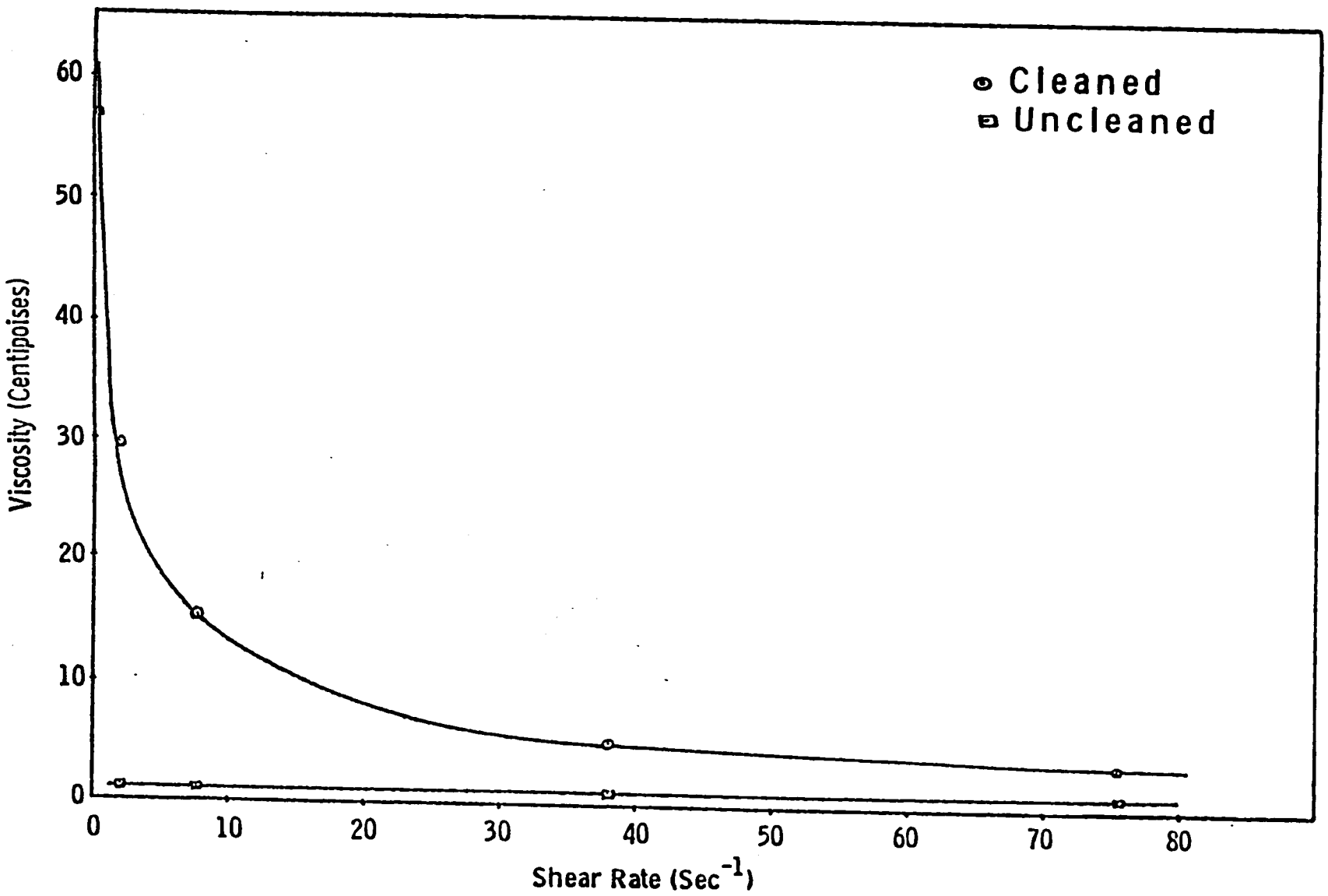


Fig. 17. Variation of Viscosiy with Shear Rate Latex 1.

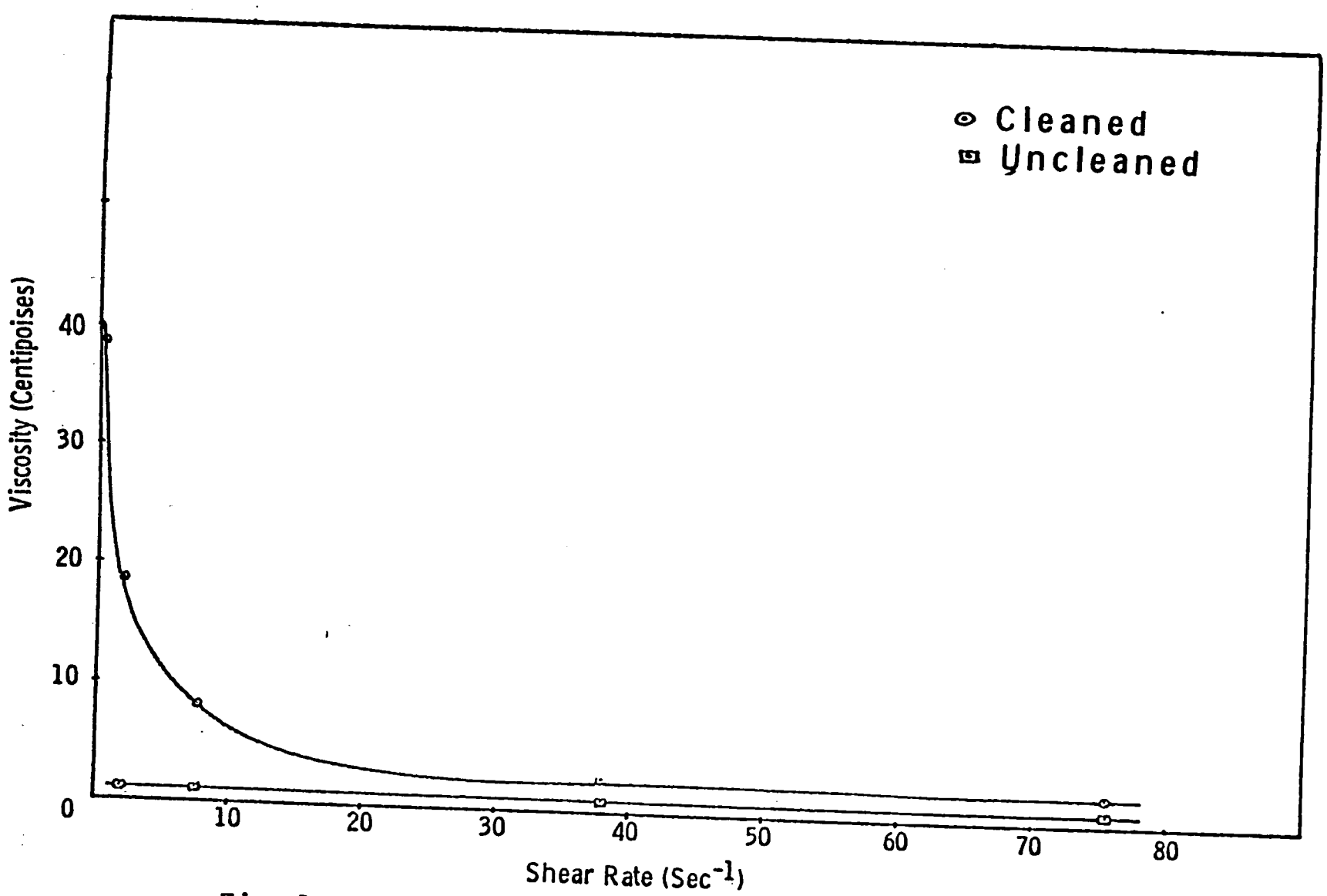


Fig. 18. Variation of Viscosity with Shear Rate Latex 3.

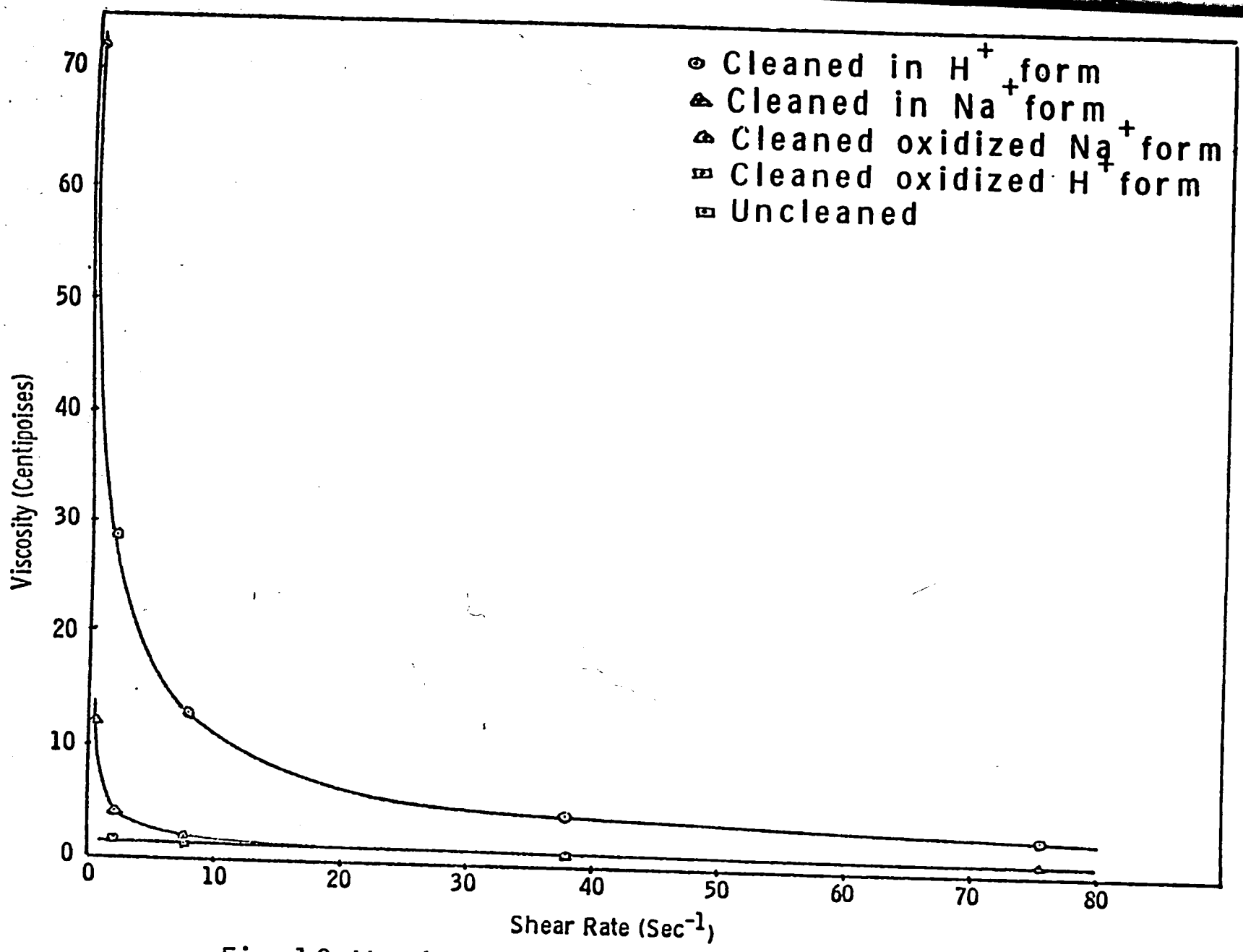


Fig. 19. Variation of Viscosity with Shear Rate Latex 2.

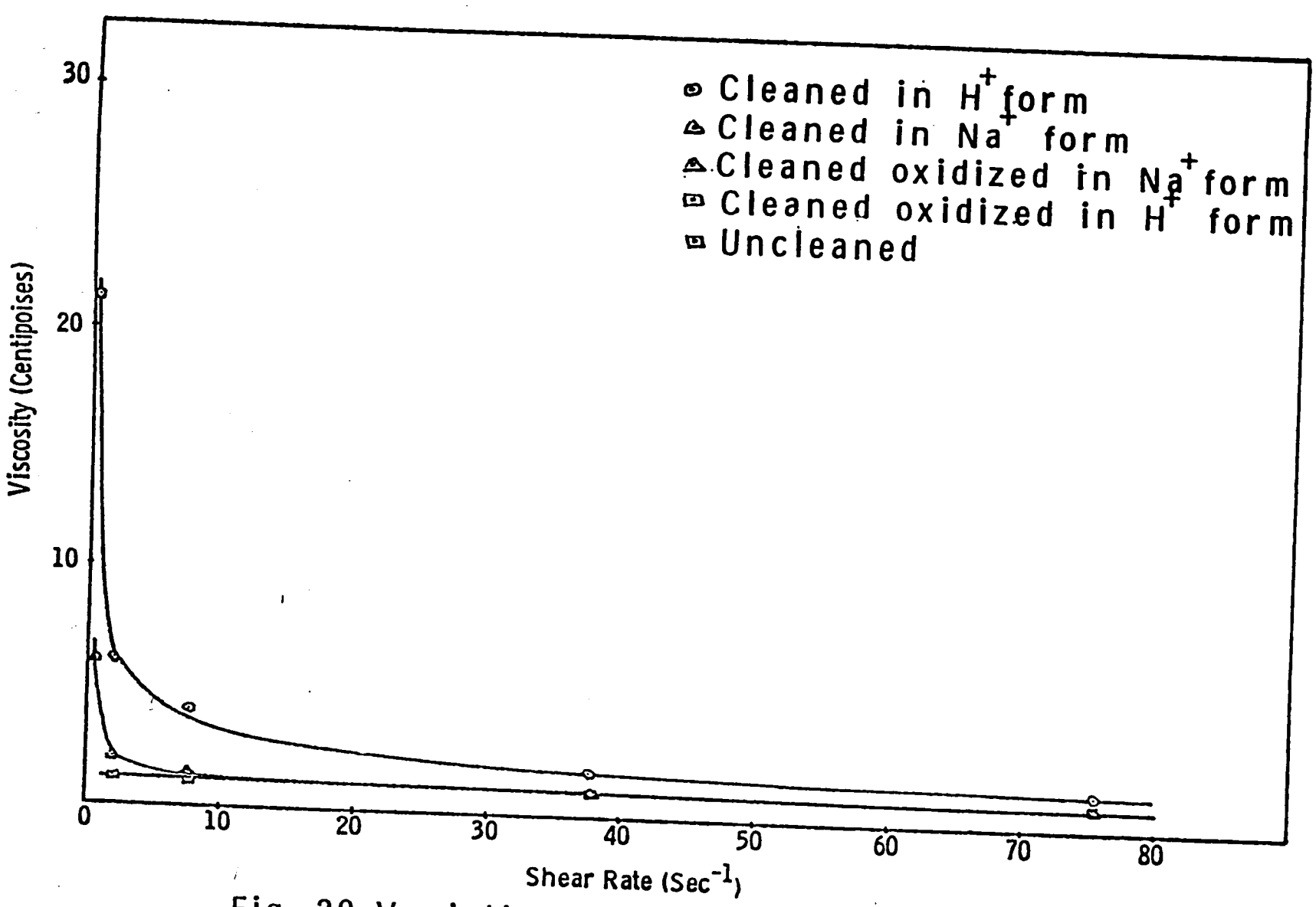


Fig. 20. Variation of Viscosity with Shear Rate Latex 4.

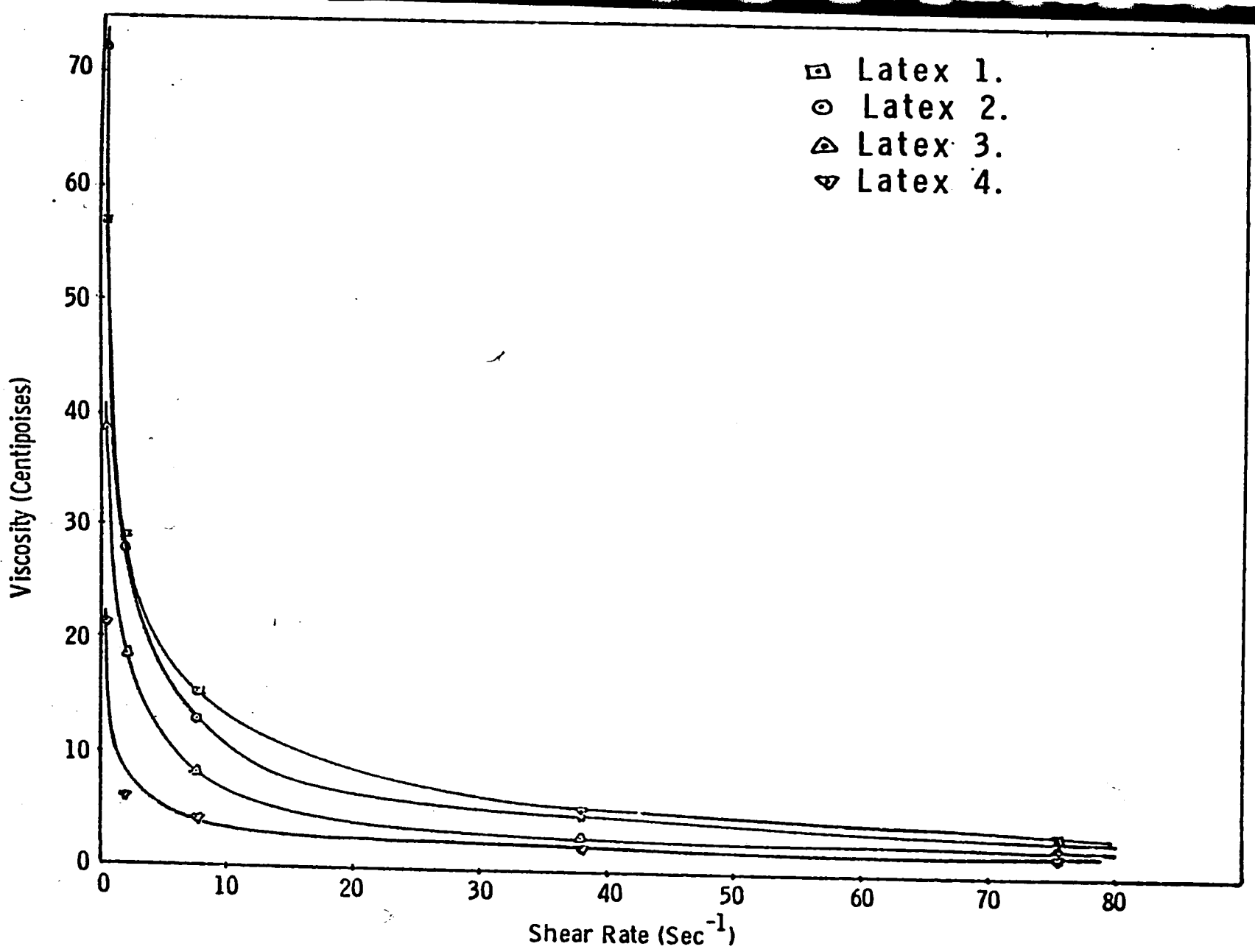


Fig. 21. Variation of Viscosities with Shear Rate leaned Latexes.

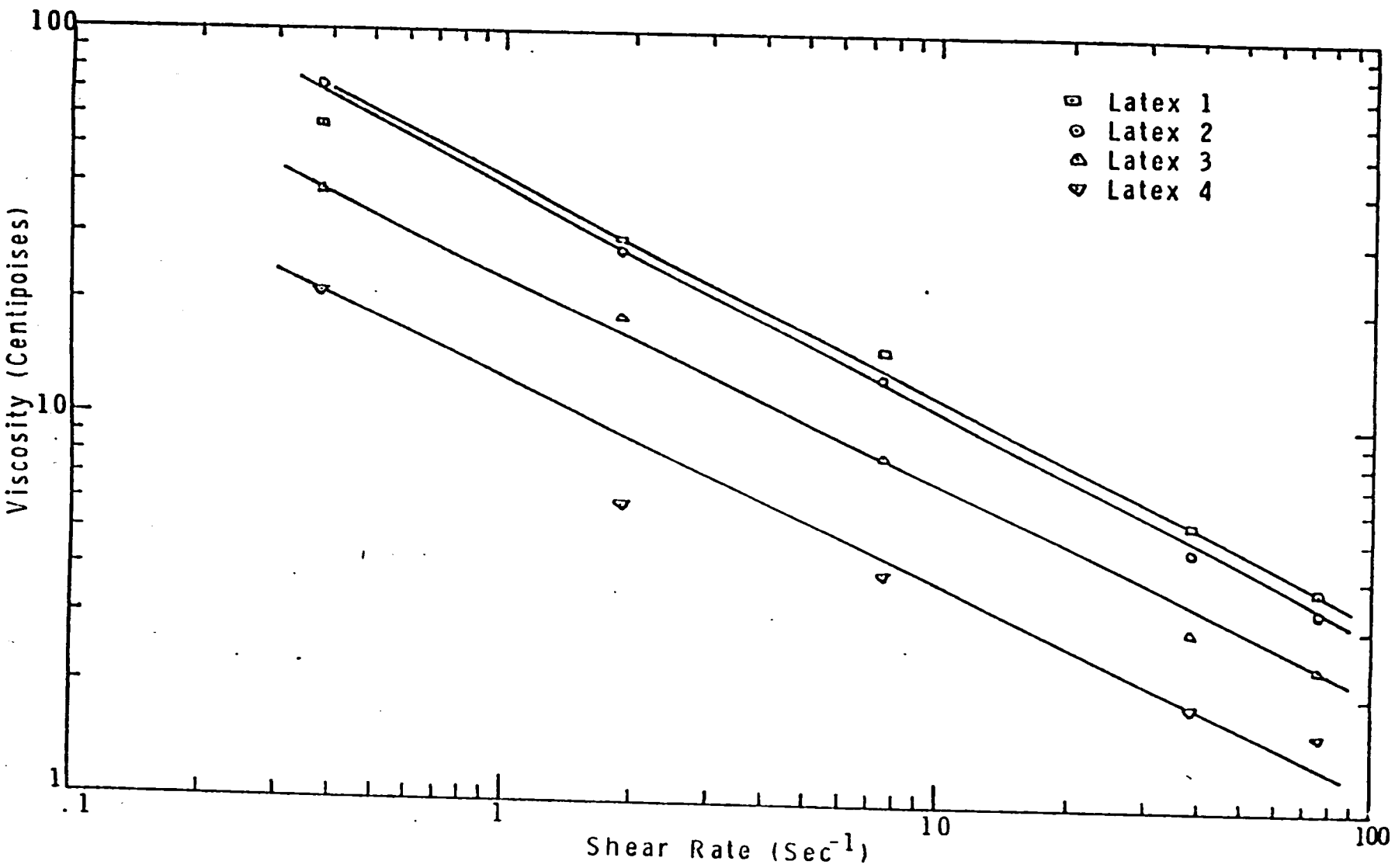


Fig. 21. Variation of Viscosities with Shear Rate

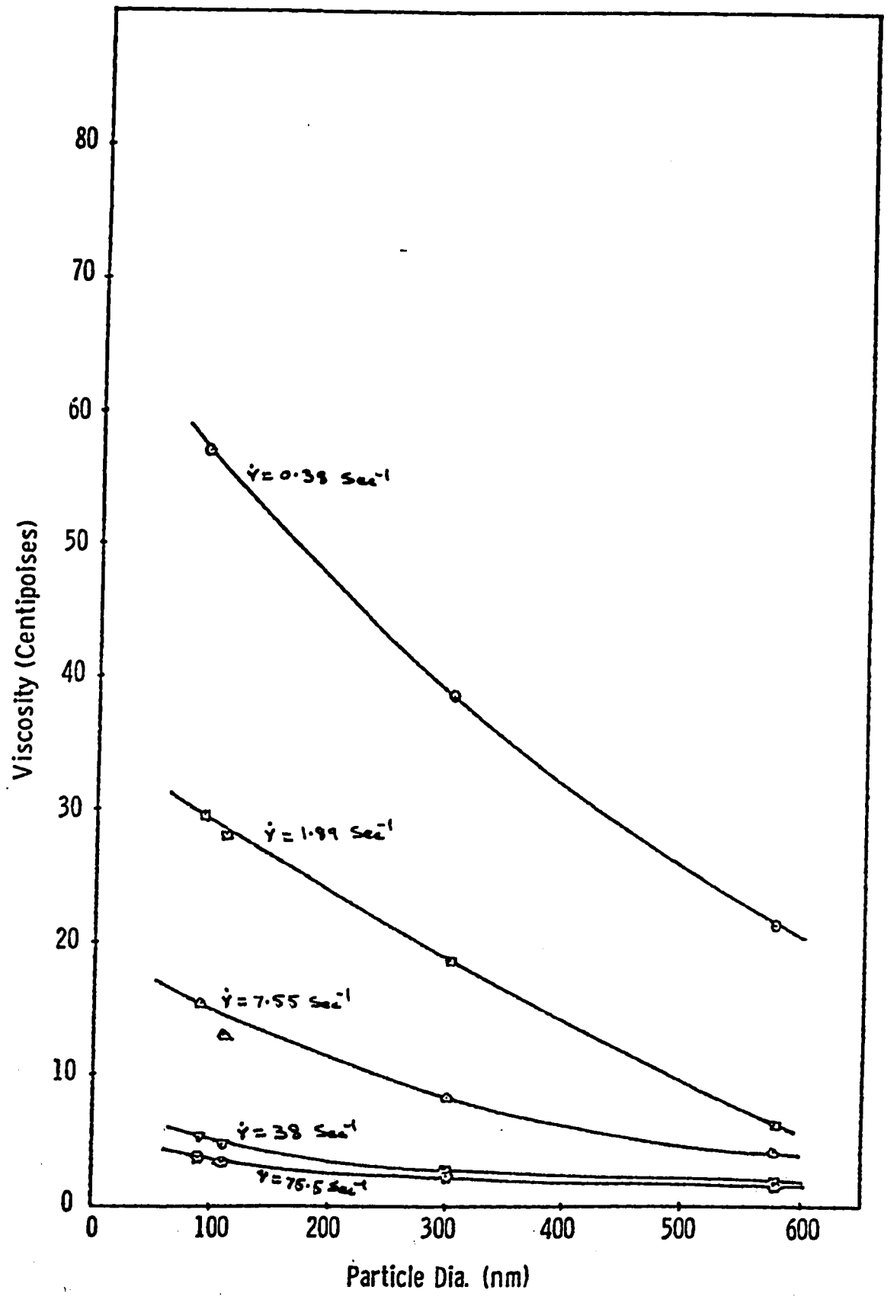


Fig. 22. Variation of Viscosities with Particle size at different Shear Rates.

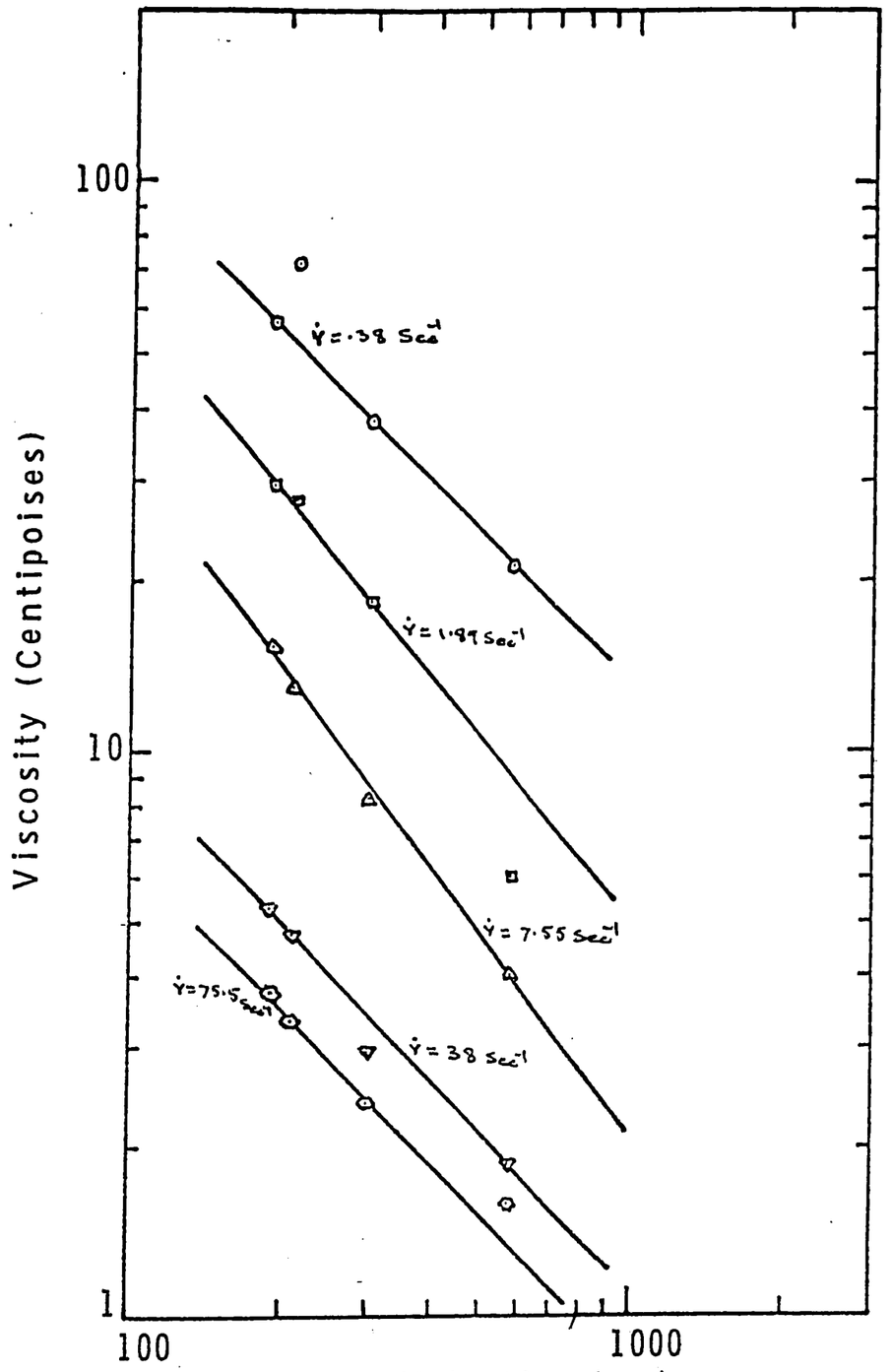


Fig. 22. Variation of Viscosities with Particle size at different Shear Rates.

earlier. However, after oxidation, the double layer interaction did not appear and viscosities did not change. This indicates that the presence of carboxylic groups resists the expansion of the electrical double layer by some ionic mechanism. Most probably, the carboxylic groups were completely undissociated and the latexes, after oxidation, were stabilized by remaining, unoxidized during oxidation process, sulfate endgroups. This also explains the resulting flocculation during oxidation process with increased amounts of $K_2S_2O_8$. Increased amounts of $K_2S_2O_8$ presumably oxidized all the sulfate and hydroxyl groups present at the particle surfaces and the resulting latexes had only carboxyl groups, which were undissociated, and did not respond towards the stability of the latexes. This behavior of sulfate and carboxylic groups was expected and can be shown in the following reactions:

$$\sim SO_4H \rightleftharpoons \sim SO_4^- + H^+ \qquad (1)$$

$$\sim COOH \rightleftharpoons \sim COO^- + H^+ \qquad (2)$$

Sulfate groups are more likely to be dissociated but the carboxylic groups are not, the equilibrium of the reaction (2) can be shifted to the right-hand side if the H^+ of the carboxyl group is replaced by Na^+ as

$$\sim COONa \rightleftharpoons \sim COO^- + Na^+ \qquad (3)$$

$$\sim SO_4Na \rightleftharpoons \sim SO_4 + Na \qquad (4)$$

The H^+ ions of the sulfate and carboxyl groups latexes 2 and 4 were replaced by Na^+ ions by excessive ion exchanges between latexes and Dowex

50W in Na^+ form. The complete exchange of H^+ to Na^+ was verified by conductometric titration after ion exchange process. Conductometric titration curves did not show any endpoints. Viscosity measurements of these latexes were carried out. Results are shown in Tables 9 and 10 (pages 64-64). Viscosities of the oxidized and unoxidized latexes were the same at all the shear rates and the viscosity behavior was non-Newtonian at low shear rates. Exchange of H^+ to Na^+ reduced the viscosities of the original unoxidized latex and increased the viscosities of the oxidized, carboxylated, latex. Results of the unoxidized latex were not in agreement with the ionic mechanism; that is, latex with Na^+ should give greater viscosity compared to one in H^+ form. Protons being held strongly close to SO_4^- should have smaller interactions of the double layers compared to weakly held Na^+ ions. Except for these results, the rest of the viscosity data is in agreement with the equilibrium reactions shown above.

Figure 22 shows the variations of viscosities with particle size at five different shear rates.

From the results of the viscosities of the oxidized latex and the results of oxidation process, it can be concluded that latex systems with sulfate and carboxyl groups at the particle surfaces provide a low viscosity latex; however, completely carboxylated latexes may not be stable when freed from adsorbed emulsifier and electrolytes. From the fact that carboxylic groups are easily dimerized, as in acetic acid, or they may interact, as in di- and tri-carboxylic acids, it is possible that the carboxylic groups present at the latex particle surfaces may be interacting each other and destabilizing the system.

The role of hydroxyl groups in the stability of the latexes having sulfate and hydroxyl groups is also not clear. When the hydroxyl groups changed to carboxyl groups (sulfate groups remaining about the same in number), latex viscosity changed significantly. Further studies should be done to examine the effect of OH groups on the stability of latexes.

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